Cambridge University Press
978-0-521-66649-7 - Orbitals in Chemistry: A Modern Guide for Students
Victor M. S. Gil
Excerpt
More information

1

Energy, probability and electrons

1.1 Energy quantization

The interpretation of chemical phenomena, and hence the development of chemistry, owes a great deal to two fundamental concepts: *energy* and *probability*. The scientific idea of energy only emerged during the nineteenth century, whereas the notion of probability is at least two centuries older. In modern chemistry, there is hardly any field which does not depend upon one or both of these basic concepts, quite often coupled to each other. Important examples where energy and probability converge simultaneously are the second law of thermodynamics and entropy (in the field of chemical transformations), and quantum chemistry and orbitals (in the field of structure of atoms and their groupings). Orbitals are the main subject of this book. In so far as the orbital concept is essential to the study of the structure of matter it also lies in the realm of physical properties – such as electric, magnetic, spectroscopic and related properties – and of chemical behaviour of substances, from both the point of view of kinetics and thermodynamics. As we will briefly see below, the links between the fields from which the two previous examples were drawn have long been established; especially the historical role played by thermodynamics in the foundations of our knowledge about matter and light is recalled.

Orbitals are mathematical functions of the coordinates of each electron in atoms, molecules and other atomic aggregates; we will see that they carry the dimensions $[\text{length}]^{-3/2}$. They contain information on the *probability distribution* for each electron in space and correspond to certain electronic *energy values*. There are two most significant non-classical features which concern the energy of bound electrons. One is that not all values of energy are allowed: *energy quantization*. The other is the so-called *exchange energy* which is a consequence of the indistinguishability of electrons. In addition,

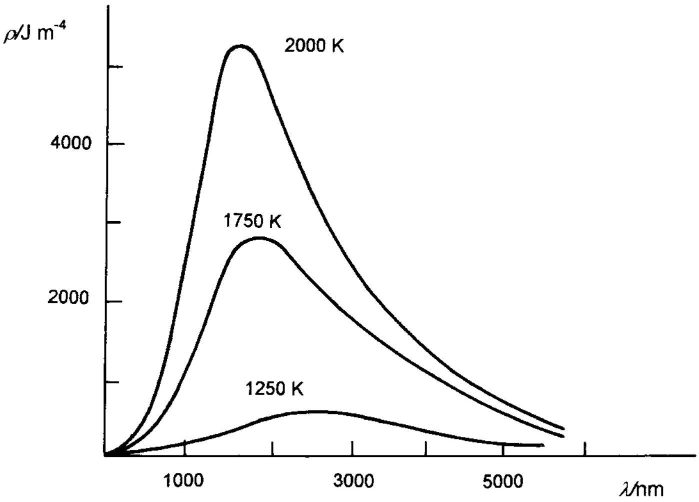

Fig. 1.1 Distribution of the energy output for a black-body (the ideal case of a body that neither reflects nor transmits light; it just absorbs or emits) at different temperatures as a function of wavelength.

our knowledge of the position and momentum of electrons is affected by the *Heisenberg indeterminacy principle*.

The concept of energy quantization has its roots in two kinds of experimental data gathered during the second half of the nineteenth century, both related to light: (a) the discontinuous emission spectra of gaseous elements; and (b) the distribution of the light intensity emitted by heated bodies as a function of wavelength for various temperatures (the so-called black-body) (Fig. 1.1).

The discrete wavelengths λ of the emission spectra were found by the end of the nineteenth century to be reproduced by a simple empirical formula, the Balmer–Rydberg equation:

$$1/\lambda = \mathcal{R}(1/n_1^2 - 1/n_2^2) \tag{1.1}$$

where $\mathcal{R} = 1.097 \times 10^5\ \mathrm{cm}^{-1}$ is a constant (the Rydberg constant) and n_1 and n_2 ($n_1 < n_2$) are integer numbers. At about the same time (1890), the German physicist Max Planck (1858–1947, 1918 Nobel laureate in Physics) found another empirical formula which reproduces the density of radiating energy due to a black-body, as a function of frequency (ν) and temperature (T):

$$\rho(\nu, T) = A\nu^3/(\mathrm{e}^{B\nu/T} - 1) \tag{1.2}$$

where A and B are constants.

Cambridge University Press
978-0-521-66649-7 - Orbitals in Chemistry: A Modern Guide for Students
Victor M. S. Gil
Excerpt
More information

The strange results summarized in Eq. (1.1) were in apparent conflict with thermodynamic data, especially with the measured heat capacities of gaseous elements. Meanwhile, Planck, taking advantage of his experience in thermodynamics, sought an explanation of Eq. (1.2) on the basis of the statistical interpretation of entropy that had been developed in 1896 by another Austrian physicist, Ludwig E. Boltzmann (1844–1906). Following previous ideas, Planck began by considering the atoms at the surface of a black-body as oscillators capable of absorbing and emitting light. In his studies and as a mathematical convenience, Boltzmann had often begun by considering the energy in small discrete amounts and only at the end of his analysis allowed this discontinuity to be removed. Planck used a similar treatment and considered discrete values $0, h\nu, 2h\nu, 3h\nu, \ldots$ (more or less populated according to the temperature) for the energies of the atomic oscillators, ν being the frequency of the oscillation and h a constant that, at the final stage, should be set equal to zero to allow all vibrational energies to be taken into account. It was then found by Planck that agreement with experiment (that is, Eq. (1.2)) could only be reached if h remained non-zero and was set equal to 6.63×10^{-34} J s. The theoretically derived counterpart of Eq. (1.2) is

$$\rho(\nu, T) = (8\pi h\nu^3/c^3)/(\mathrm{e}^{h\nu/kT} - 1) \tag{1.3}$$

where c is the speed of light in vacuum and k is the Boltzmann constant. The constant h was later, very properly, named the Planck's constant. Meanwhile, $h\nu$, the difference between successive energy values, was called a *quantum* of energy for the electromagnetic oscillators. The concept of energy quantization was born (with important contributions from the work of other physicists, mainly Franck and Hertz). Although the energy difference $h\nu$ between successive energy values was later found to be in agreement with the quantum-mechanical treatment of diatomic molecules as harmonic oscillators, the minimum value, zero, considered by Planck should be replaced by $h\nu/2$, the so-called zero-point energy. For an harmonic oscillator, the allowed vibrational energy values are $h\nu/2, 3h\nu/2, 5h\nu/2, \ldots$.

In 1905, Albert Einstein (1879–1955, 1921 Nobel laureate in Physics), born in Germany and later a naturalized American, having overcome some initial disbelief concerning the energy quantization of oscillators, extended this idea to electromagnetic radiation itself. Radiation carries energy in discrete amounts – *quanta* – each quantum or ‘particle’ of radiating energy being

$$E = h\nu \tag{1.4}$$

where ν is now the frequency of the electromagnetic radiation. It has been recognized that Einstein became much more enthusiastic about Planck's theory than the author himself, who had great difficulty in discarding the principles of mechanics – now called classical mechanics – on which he had been brought up. The 'particles' of radiating energy were some years later named *photons* by the American chemist Gilbert N. Lewis (1875–1946). Thus, the energy of η photons corresponding to a given frequency ν is

$$E = \eta h\nu. \tag{1.5}$$

The photon model explained more than the black-body radiation. One of the first great achievements of the new theory of light was the interpretation of the *photoelectric effect*. The difference between the energy $h\nu$ of the incident photon and the minimum energy I necessary to remove an electron from the structure it belongs to (ionization energy, in the case of gaseous samples; work function, in the case of condensed phases) appears as kinetic energy $mv^2/2$ of the ejected electron:

$$h\nu = I + mv^2/2. \tag{1.6}$$

Thus, electron ejection requires a minimum frequency ν, it being irrelevant to have an intense source of light (many photons per unit of area) if the frequency is less than that minimum. However, the more intense the beam of light of appropriate frequency the greater the number of electrons ejected, by a one-to-one photon–electron interaction.

The proposal of Einstein was not accepted easily. Even as late as 1913, Planck himself, when joining other distinguished German physicists in recommending Einstein's appointment to the Prussian Academy of Sciences, would write

> ...That he may sometimes have missed the target in his speculations, as, for example, in his hypothesis of light quanta, cannot really be held against him, for it is not possible to introduce fundamentally new ideas, even in the most exact sciences, without occasionally taking a risk.

The idea of energy quantization was brought into chemistry with the application of quantum theory to the electronic structure of atoms in 1913 by the Danish physicist Niels Bohr (1885–1962, 1922 Nobel laureate in Physics). At the time, Bohr was working in the laboratory of the New Zealand physicist Ernest Rutherford (1871–1937, 1909 Nobel laureate in Chemistry) in England, a short time after the nuclear structure for the atom had been established by Rutherford and his co-workers. Classical electromagnetic theory predicted that the electrons around the nucleus, because they are being accelerated (centripetal acceleration), should radiate energy and thus should gradually approach the nucleus, emitting energy in a continuous manner, until the final collapse into the nucleus. However, it was known that atoms are not only stable entities but also, when previously excited, they radiate energy in discrete amounts. Then, inspired by the quantum theory of Planck, Bohr was forced to admit that the electrons in atoms exist in *stationary energy states*, with a well-defined energy, which they can only leave by either absorption or emission of certain discrete values of energy.

In such states, the electrons (charge $-e$ and mass m_e) would have circular orbits (radius r) around the nucleus, undergoing transitions between orbits through either absorption or emission of energy. In particular, for the hydrogen atom, the total energy of the electron in circular orbit (the kinetic energy in the rest frame of the nucleus, $m_e v^2/2$, plus the potential energy associated with the electron–nucleus attraction, $-\boldsymbol{k}e^2/r$) could only have certain values. In order to obtain these values, Bohr began by assuming, as was done by Planck for the radiation of the black-body, that the energy emitted by the excited H atom was given by

$$E = n'h\nu' \tag{1.7}$$

with n' a positive integer and ν' a frequency characteristic of the motion of the electron around the nucleus. The crucial problem was then to relate ν' with the angular velocity of the electron circular motion. Bohr made some conjectures that, however, led to an impasse. When, almost by chance, the Balmer–Rydberg equation (1.1) was made known to him, the solution became clear and the following formula could be established for the possible values of energy of the electron in the H atom:

$$E_n = -(2\pi^2 e^4 m_e)/h^2 n^2 \tag{1.8}$$

with $n = 1, 2, 3, \ldots$ a *quantum number*.

This energy quantization would imply, too, quantization of the angular momentum of the electron $m_e vr$:

$$m_e vr = nh/2\pi. \tag{1.9}$$

Contrary to what is often found in books, Eq. (1.9) was not the starting point for the energy quantization expression (1.8), but the other way round. (For discussion of this point and the presentation of the Bohr model, see, for example, refs. 1 and 2.)

Cambridge University Press
978-0-521-66649-7 - Orbitals in Chemistry: A Modern Guide for Students
Victor M. S. Gil
Excerpt
More information

However, the theory presented several limitations and could not explain the spectra of atoms other than monoelectronic atoms. Bohr himself would recognize the need for a new theory and, indeed, would contribute to it. In particular, it is noted that, although Eq. (1.8) is reproduced by quantum mechanics, the angular momentum of the electron is not given by Eq. (1.9); in particular, the minimum value possible is zero and not $h/2\pi$ as required by Eq. (1.9).

1.2 The wave–particle duality, observations and probability

The photon theory of light and Eq. (1.5) received additional confirmation when, in 1923, the American physicist Arthur H. Compton (1892–1962, 1927 Nobel laureate in Physics) discovered the effect that would bear his name: *the Compton effect*. When X-rays interact with electrons, the scattered radiation, after transferring some energy to stationary electrons (which are accelerated by the electric field of the radiation), has a slightly higher wavelength. In contrast with classical physics, this increase $\Delta\lambda$ depends only on the angle θ through which the radiation is deflected, being independent of the initial wavelength:

$$\Delta\lambda = \lambda' - \lambda = \lambda_c(1 - \cos\theta). \tag{1.10}$$

The constant $\lambda_c = 2.425$ pm is called the *Compton wavelength* of the electron. The wavelength shift given by Eq. (1.10) can be easily reproduced theoretically if the interaction between the radiation and the electron is considered as a collision between two particles in which the energy and the linear momentum are conserved (conservation of momentum in the incident direction and in the direction perpendicular to it). These particles are a photon of energy $h\nu$ and linear momentum $p = h\nu/c = h/\lambda$ and a stationary electron of mass m_e which acquires velocity v (Fig. 1.2). It is then found

$$\lambda_c = h/m_e c = 2.425\,\text{pm}. \tag{1.11}$$

Equation (1.5) establishes a bridge between a description of light as an (electromagnetic) wave of frequency ν and as a beam of η energy particles. If phenomena related to time averages, such as diffraction and interference, can be easily interpreted in terms of waves, other phenomena, involving a one-to-one relation such as the photoelectric and the Compton effects, require a description based on corpuscular attributes. This wave–particle duality reflects the use of one or the other description depending on the experiment performed, while no experiment exists which exhibits both aspects of the duality simultaneously.

Cambridge University Press
978-0-521-66649-7 - Orbitals in Chemistry: A Modern Guide for Students
Victor M. S. Gil
Excerpt
More information

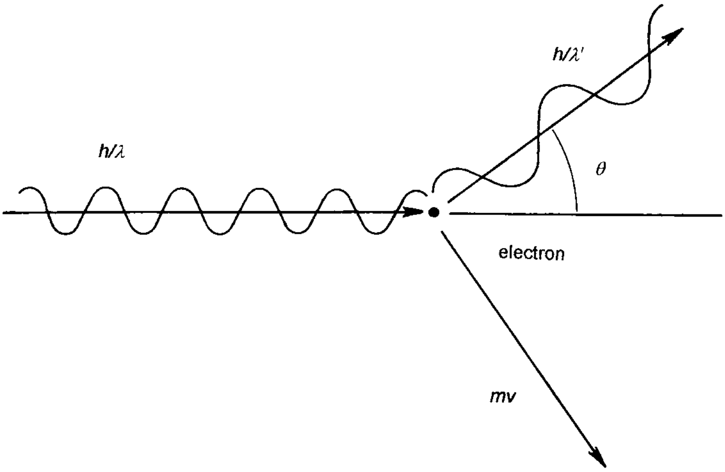

Fig. 1.2 Conservation of linear momentum in the Compton effect.

The form $p = h\nu/c = h/\lambda$ for the linear momentum of a photon can be obtained by combining the expression for the energy of a photon $E = h\nu$ and the expression $E = m_{\text{ph}}c^2$ which defines the relativistic mass of the photon, m_{ph}, provided that the linear momentum of a photon is made equal to $m_{\text{ph}}c$ by analogy with the classical expression mv for the linear momentum of a particle.

Strongly influenced by the interpretation of the Compton effect, the French physicist Louis Victor, Prince de Broglie (1892–1987, 1929 Nobel laureate in Physics), suggested in his doctoral thesis in 1924 that the wave–particle duality for photons could be extended to any particle of momentum $p = mv$ which, *somehow*, would then have a wavelength – the *de Broglie wavelength* – associated with it and given by

$$\lambda = h/p. \tag{1.12}$$

Indeed, considering that photons are rather peculiar particles in that they have zero rest mass and can exist only when travelling at the speed of light, it seems reasonable that the wave associated with the motion of any particle should become more and more apparent as the mass decreases, rather than the wave coming into existence suddenly when the rest mass vanishes.

This was a revolutionary and quite nebulous suggestion, not easily accepted at the time. If it was not for the intervention of Einstein, excited with the proposal, Louis de Broglie would most likely have failed his doctoral examination. Louis de Broglie found support for his hypothesis and attempted to clarify the 'wave characteristics' of a moving electron by

Cambridge University Press
978-0-521-66649-7 - Orbitals in Chemistry: A Modern Guide for Students
Victor M. S. Gil
Excerpt
More information

successfully reproducing the Bohr expression (1.9) for the quantization of the angular momentum of the electron in the H atom. By trying to adjust waves to a circular orbit, it is found that destructive interference between waves in successive cycles is only avoided if the orbit perimeter is a whole number of wavelengths: $2\pi r = n\lambda$. Associating Eq. (1.12), and putting $p = m_e v$, Eq. (1.9) is then reproduced.

The 'associated wave' of the de Broglie relation was later replaced by the quantum-mechanical wavefunction of the particle. But the experimental proof of the de Broglie hypothesis and his quantitative relation appeared in 1927 with the first observations of diffraction of electrons by C. Davisson and L. Germer in America and by G.P. Thomson in Great Britain, using a nickel crystal and a gold foil, respectively. These results were found to be analogous to those obtained when using X-rays having wavelengths equal to the de Broglie wavelengths for electrons. It is interesting to note that, whereas J.J. Thomson showed at the end of the nineteenth century that the electron 'is a particle', and received the 1906 Nobel prize in Physics mainly for that, his son G.P. Thomson showed that it 'is a wave', and got the same prize in 1937 (shared with Davisson). In 1932, the occurrence of diffraction of helium atoms and hydrogen molecules by crystals was also found to be in agreement with the de Broglie relation.

The interpretation given by de Broglie for the quantization of the angular momentum of the electron of H, in the Bohr model, assumes *in some sense* that the electron can interfere with itself. Although any diffraction experiment always presupposes a large number of particles, it is not necessary that all the particles are considered at the same time; diffraction can still be obtained with a sequence of a large number of particles, one at a time. For example, a diffraction pattern is gradually built up as photons or electrons pass through two slits which are separated by a distance of the order of the wavelength of the particles (Fig. 1.3). In this sense, it can be said that each particle interferes with itself (refs. 3–5).

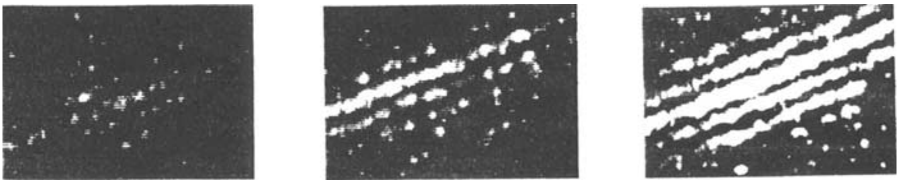

Fig. 1.3 Gradual genesis of an electron interference pattern in a double-slit experiment, with electrons reaching the detector one at a time. (Adapted with permission from ref. 5.)

This result clearly points to the impossibility of considering that the particle passes through one slit and not through the other; it seems 'to pass through both'. In other words, we can only say that it has 50% probability of passing through one slit and 50% of passing through the other. A bridge between the *wave characteristics* of small particles and *probability* is beginning to arise. Simultaneously, the notion of trajectory – from one slit to the screen or detector – no longer applies.

In contrast to this, for macroscopic particles, it is possible to identify the slit through which they pass; trajectories can then be defined and no interference occurs. The passages through each slit are then independent events and the probability of particles striking a given point on the screen, in a certain time interval, is just the sum of the probabilities corresponding to passage through slit 1 and through slit 2.

The interference of microscopic particles leads to a diffraction pattern with deviations with respect to the mere sum of the individual probabilities. The two events are no longer independent. If we wish to state in advance where the next particle will appear, we are unable to do so. The best we can do is to say that the next particle is more likely to strike in one area than another. *A limit to our knowledge*, associated with the wave–matter duality, becomes apparent. In the double-slit experiment, we may know the momentum of each particle but we do not know anything about the way the particles traverse the slits. Alternatively, we could think of an experiment that would enable us to decide through which slit the particle has passed, but then the experiment would be substantially different and the particles would arrive at the screen with different distributions. In particular, the two slits would become distinguishable and independent events would occur. No interference would be detected, that is, the wave nature of the particle would be absent. In such an experiment, in order to obtain information about the particle position just beyond the slits, we would change its momentum in an unknown way. Indeed, recent experiments have shown that interference can be made to disappear and reappear in a 'quantum eraser' (ref. 6 and references therein).

This discussion extends to electrons, and small particles in general, what we have already found for photons, that is, the appearance of electrons behaving as classical particles or as a wave depends on the experiment being performed. On the other hand, it illustrates a basic feature of microsystems: there is an unavoidable and uncontrollable interaction between the observer and the observed. No matter how cleverly one devises an experiment, there is always some disturbance involved in any measurement and such a disturbance is intrinsically indeterminate (see also Section 1.3).

However, the situation concerning the limits to our knowledge depicted above is not as desperate as it would seem. The fact that we can say that the next particle in a double-slit diffraction experiment is more likely to strike in one area of the screen than another points to the existence of a certain 'determinism' in the statistical result for a large number of identical experiments. We need to consider not each individual microsystem but a *statistical ensemble*, that is a great number of non-interacting replicas of a given microsystem which enable a large number of identical experiments to be performed; or, alternatively, we need to repeat the same experiment with the same microsystem, always in the same conditions. For example, one mole of H atoms corresponding to 6.022×10^{23} atoms all in the same electronic state is an ensemble for measurements about the electron. This characterization of a collection of microsystems in the same conditions is called *state preparation*.

Each individual measurement of any physical quantity yields a value A. But, independently of any possible observation errors associated with imperfect experimental measurements, the outcomes of identical measurements in identically prepared microsystems are not necessarily the same. The results fluctuate around a central value. It is this collection or spectrum of values that characterizes the *observable* A for the ensemble. The fraction of the total number of microsystems leading to a given A value yields the probability of another identical measurement producing that result. Two parameters can be defined: the *mean value* (later to be called the 'expected value') and the *indeterminacy* (also called uncertainty by some authors). The mean value $\langle A \rangle$ is the weighted average of the different results considering the frequency of their occurrence. The indeterminacy ΔA is the standard deviation of the observable, which is defined as the square root of the dispersion. In turn, the dispersion of the results is the mean value of the squared deviations with respect to the mean $\langle A \rangle$. Thus,

$$\Delta A = \langle (A - \langle A \rangle)^2 \rangle^{1/2} \tag{1.13}$$

which is a statistically meaningful expression of precision or reproducibility of measurements. (For a discussion of precision and accuracy in measurements, see, for example, ref. 7.)

1.3 Wavefunctions and the indeterminacy principle

Much of what has been said earlier lies at the foundations of the new mechanics which began with the work of the German physicist Max Born