Coulson's
Valence

ROY McWEENY

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Preface

The greater part of *Valence*, in its earlier editions, was written before 1950. It contained the first broad and authoritative account of molecular orbital ideas in the quantum theory of valence and it was written for chemistry students of modest mathematical attainment. It was for many years unrivalled, was translated into six languages, and won the affection of students and their teachers the world over. Its impact on chemistry was enormous; but by 1975 it was a great book grown old. Even ten years after the 1961 edition the need for a complete revision and rewriting of almost the whole book was already urgent. Its author had no doubts about how much would be required; sadly, he did not live to take on the task.

In this Third Edition I have tried to reconstruct the book broadly as, I believe, its original author would have wished. My personal links with Charles Coulson lasted from the days I spent as a research student in Oxford, during 1946–48, until a few days before his death in 1974, a period which took theoretical chemistry from the era of calculating machines with handles to the age of the computer. During that time he never lost faith in what he called 'primitive patterns of understanding' and had he lived to write a Third Edition there is no doubt that this faith would have remained evident. In trying to update the book, in the face of the fearsome mathematical developments of the last twenty-five years, I have done my best to capture the spirit of the original, to emulate its high standards of clarity and style, and to avoid overburdening the text with equations whenever a pictorial argument would suffice.

The plan of the book follows quite closely that of previous editions. Chapter 1 has been little changed, except for the addition of two short sections to provide a more modern perspective on valence theory. Chapters 2 and 3 have been substantially rewritten to give fuller coverage of the basic ideas of quantum mechanics, thus keeping the book self-contained; only one section (§3.10) is of a more difficult nature and this may be passed over on first reading with no great loss. In subsequent chapters some material has almost disappeared whilst other sections have expanded considerably to take account of recent developments. In particular, theories of chemical reactivity now receive a whole chapter and the treatment of energy band theory has been extended in view of the growing importance of solid-state chemistry. A final chapter has been added for readers who may want to obtain some appreciation of current methods of performing electronic structure calculations. The three appendices are also new and problems have been set at the end of chapters. SI units have been employed throughout.

The literature of valence theory is now enormous and my debt to others will be apparent; but this is a book for chemistry students and their teachers, not for experts in molecular quantum mechanics, and I have therefore been sparing in references to original work. The ones I have given merely provide access points to some of the main lines of development and indicate the origin of the main ideas and concepts. I have not attempted to provide a survey of theories and calculations.

I hope *Coulson's Valence* will be a worthy successor to the two earlier editions of *Valence*. In a real sense it is the result of a collaboration, though unhappily I alone must bear full responsibility for the errors and obscurities which surely remain. To repeat the words of an earlier Preface 'I should be grateful to be told of places where I could do better'.

I am grateful to Mrs. Eileen Coulson for encouraging me to undertake this revision and for kindly putting at my disposal annotated personal copies of previous editions, along with an English text of the section on *Compounds of the rare gases* prepared for the German edition; the penetrating comments in a familiar scribble gave me constant reassurance. I am grateful, too, to Dr. P. W. Atkins for painstakingly reading the whole manuscript and sending a long list of critical remarks which he modestly described as 'puny and piffling' but which were nonetheless valuable; to those authors and publishers who have allowed me to reproduce material; Oxford University Press for editorial help and for gently keeping up the pressure when my spirits were flagging; and to Mrs. S. P. Rogers for turning my handwritten copy into immaculate typescript.

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1

Theories of valence

1.1. Essentials of any theory of valence

This book is concerned with the theory of valence. It is therefore useful first to recall some of the chief phenomena to be explained. We are not concerned primarily with the details of molecular structure, interesting as these may be, but rather with the main principles of molecule formation, for in so far as the details are significant, they must follow from the basic principles.

In the first place, we must show why molecules form at all. Why, for example, do two hydrogen atoms come together to form a permanent and stable compound, molecular H_2, while two helium atoms do not form a corresponding He_2 (except of so transitory a character that it cannot be called a chemical species)? Secondly, why do atoms form compounds in definite proportions? From the earliest days of Gay-Lussac and Berzelius the law of multiple proportions has insisted on the fundamental character of the combining ratio for different atoms. But the picture of an atom which resulted from the work of subsequent investigators such as Frankland and Kekulé was rather like that of a tiny sphere on the surface of which a certain number of 'knobs' (i.e. valences) determined the number of other atoms that could be directly attached to it. This picture is inconsistent with known chemical behaviour; it is true that H (with one knob) would combine with another H to form H_2 but not with *two* more H's to form H_3—this being the 'saturation' property of chemical valence—but how could we account for the existence of *both* CO and CO_2? A satisfactory theory must explain not only the numerical ratios of the numbers of atoms combining to form a molecule but also the *variability* of such ratios (i.e. the existence of *multiple* valences) and the relationship of such behaviour to the position of an atom in the periodic table.

Thirdly, a complete theory of valence should be able to account for the stereochemistry of molecules. The shapes and dimensions of molecules can now be inferred with increasing precision by a wide variety of spectroscopic and other physical techniques, and such knowledge places new demands on a theory of valence. Why, for example, do the H—C—H angles in methane (CH_4) all have the tetrahedral value of 109° 28′, while in chloroform ($CHCl_3$) the corresponding Cl—C—Cl angles are increased to about $110\frac{1}{2}^\circ$? Why is CO_2 linear, while H_2O is V-shaped?

A good theory of valence should also give a *unified* explanation of these three main aspects of molecular structure; it should show *if* an atom has the

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power to attach another atom, or group, to itself, *how many* such atoms it may attach, and *in what geometrical arrangement.*

Finally, new physical techniques give a very intimate knowledge of the nature and properties of bonds, of their shapes and individual features, far beyond that implied by drawing a single line to represent a single bond and two lines for a double bond. These intimate details should also be accounted for by the theory.

1.2. Electronic character of valence

In a profound sense the description of bonds in a molecule is simply the description of the distribution of electrons around the nuclei. The early attempts to develop an electronic theory of valence were based on geometrical models in which the electrons were regarded as static point charges placed at the corners of cubes or tetrahedra with the nuclei at the centres; they gave an interpretation of the octet rule, in which each atom achieved a configuration with eight outermost electrons located at the corners of a cube, and they suggested a connection with the periodic table introduced by Mendeleev in 1869. But such models violate a fundamental theorem in electrostatics which states that no static distribution of charges can be in stable equilibrium—the charges must be *moving*. Even the earliest ideas, going back to Berzelius (1819), of the bonding in ionic compounds suffered from this defect. The attractions among ions with dissimilar charges suggested the electrostatic origin of bonding, but some new repulsive force was then necessary to prevent the collapse of the whole structure; the equilibrium in ionic crystals could not be accounted for by electrostatics alone. In molecules such as H_2, with covalent bonds, electrostatic forces of the Coulomb type were even less able to account for the attraction between the individual electrically neutral atoms.

The first attempt at a dynamic model was due to Bohr (1913) who assumed that the electron in the hydrogen atom moved in an *orbit* around the positively charged nucleus. By applying the classical (Newtonian) laws of motion, coupled with a postulated 'quantum condition', he obtained a discrete set of permitted orbits, each with a characteristic energy. Transitions from one energy level to another then accounted almost perfectly for the emission and absorption of corresponding energy quanta of radiation, as observed in spectroscopy. But the theory broke down completely for systems with more than one electron, or with more than one nucleus (e.g. in H_2^+).

Bohr's theory failed because it applied the laws of classical physics, established by observing the motion of masses in the laboratory, to electrons and nuclei—particles so small that their motion, as classically envisaged (e.g. in a precisely defined orbit), could never actually be observed in any conceivable experiment. We cannot expect that the same laws necessarily apply at the electronic level, or even that the classical concepts retain their validity. It is now known that at this level we must employ the laws of quantum mechanics—of which one particular formulation, wave mechanics, was introduced by Schrödinger in 1926. The laws of quantum mechanics reduce to those of classical mechanics for systems of large mass† (e.g. everyday objects in the laboratory), but they also apply, with a validity and accuracy which is now beyond question, to the electrons in atoms and molecules. On the basis of quantum mechanics it is now possible in principle, and to a considerable extent in practice, to build up a coherent and complete theory of molecular structure and properties.

1.3. Importance of the energy

Broadly speaking, two atoms form a molecule because there is a lowering of the total energy when they come together. For most purposes the energy of a molecule may be regarded as the sum of an electronic energy (comprising the kinetic energy of the electrons and their potential energy, both mutual and in the field of the nuclei, calculated as if the nuclei were fixed in their equilibrium positions), together with the mutual potential energy of the nuclei and the energies of vibration, rotation, and translation of the molecule as a whole (associated almost entirely with the nuclei, with their comparatively large masses). The energy due to vibration, rotation, and translation of the molecule, although significant in spectroscopy, is normally a very small fraction of the total, and the total energy is thus almost synonymous with the electronic energy, supplemented by the Coulombic repulsion energy of the nuclei. To avoid constant explicit reference to the latter, it is convenient to include the nuclear repulsion energy as an extra term in the electronic energy; references to the total electronic energy will usually be understood in this sense, i.e. as the total energy *in the absence of nuclear motion.* This 'electronic energy' then plays the dominant role in determining molecular structures. For example, the fact that hydrogen forms diatomic aggregates such as H_2 rather than triatomic aggregates such as H_3 follows from the fact that the electronic energy of H_3 is greater than the sum of that of H_2 and H. Similarly the HOH angle in water is about $104\frac{1}{2}^\circ$ and the two OH bond lengths are each 0·096 nm because it is for these values of the internal co-ordinates of the molecule that the energy is lowest. A satisfactory theory of valence therefore must be able to show how the electronic energy depends on the positions of the nuclei, and thus to predict not only the equilibrium configuration but also how the energy changes when the molecule is distorted. This means we can obtain the restoring force in any deformation and have available all the information required for calculating the normal modes of vibration. Consequently, the theory of valence has immediate implications for infrared and Raman spectroscopy (in which characteristic frequencies depend on vibrational force constants) and in the discussion of rotational fine structure (determined by moments of inertia, and hence by the positions of the nuclei) and of a multitude of other geometry-dependent effects.

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† It should be noted that the forces associated directly with the mass (i.e. *gravitational* forces) are entirely negligible for electrons. To separate the two atoms in H_2 to infinity against only their gravitational attraction, each being of mass $1{\cdot}7 \times 10^{-27}$ kg, would require about $2{\cdot}5 \times 10^{-54}$ J, but the energy actually required, as determined thermochemically, is about $6{\cdot}7 \times 10^{-19}$ J—larger by a factor of more than 10^{35}! The observed energies are thus entirely *electrical* in origin.

In discussing the formation and dissociation of molecules we are concerned with energy *differences*, usually small differences between very large quantities. Consequently, nuclear motion may sometimes need to be taken into account. The difference between the total electronic energy of the molecule (remembering that (p. 3) this conventionally includes the repulsion energy between all pairs of nuclei) and that of its component atoms is the *electronic binding energy* of the molecule. This is not the same as the experimentally observed dissociation energy (i.e. the energy required to break up the molecule into its constituent atoms) when allowance has been made for nuclear motion which, in practice, is always present. The three terms to consider are as follows: (i) the zero-point energy of vibration, which for large polyatomic molecules may reach a total value comparable with the energy required to break any one bond, though for diatomic molecules the ratio is usually of the order $\frac{1}{10}$ to $\frac{1}{20}$; (ii) the translational energy, which is equal to $\frac{3}{2}kT$ both for the original molecule and for each separate fragment; (iii) the energy of rotation of the molecule as a whole, which, except very near 0 K, is $\frac{3}{2}kT$ for a non-linear system and kT for a linear one. For a diatomic molecule the dissociation energy may be called the bond energy, since it represents the energy required to break the bond. Because of the effects (i)–(iii) this bond energy depends slightly on the temperature, though of course the electronic binding energy does not. For a polyatomic molecule we can still speak of the dissociation energy of any one bond, for this represents the energy needed to break the molecule at this bond into two fragments. However, on account of the fact that after the break-up there is often a considerable electronic rearrangement in the two parts, sometimes resulting in the recovery of quite a large amount of energy, the total energy of dissociation of a molecule is not usually the same as the sum of the separate dissociation energies of each bond. A simple example of this distinction between the total binding energy and the sum of the dissociation energies of the separate bonds is found in the water molecule H_2O. The total binding energy is about 9·49 eV, so that, if we wished, we could speak of an average bond energy of 4·75 eV. However, the energy needed to break either of the O—H bonds separately is no less than 5·18 eV. The explanation of the apparent discrepancy is that after we have broken the first O—H bond we only require 4·31 eV to break the second, and the sum of 5·18 and 4·31 is the same as the original 9·49.

There is yet one further distinction to be mentioned. Bond energies are usually inferred from heats of reaction, adjusted so as to refer to a constant pressure of 1 atm and a temperature of 25°C. These heats of reaction represent changes in the enthalpy $H = U + PV$, rather than the internal energy† U, and if, as usually happens in a dissociation, there is a change of volume, we ought to correct for the presence of the term PV.

Many of these corrections to the original electronic binding energy of the molecule would be unnecessary if all values were extrapolated to zero temperature, but such corrections are usually difficult to make with complete certainty and when made they do not appear to cause any great relative changes in bond energies. For this reason tables of bond energies given in the literature are for standard conditions of temperature and pressure, and are not therefore strictly bond energies at all! In very accurate numerical work care is needed to distinguish between energy and enthalpy, but it will not be necessary to do so in this book where we shall be concerned almost entirely with electronic binding energies.

It may serve to emphasize the relative importance of some of these energy terms if we show their values for the particular case of H_2, taken in part from Herzberg and Monfils (1960). The temperature-dependent terms are estimated for $T = 291$ K.

Some energy values for H_2

Total electronic energy of H_2	3098·3 kJ mol^{-1}
Electronic energy of two H atoms	2642·6 kJ mol^{-1}
Electronic binding energy	458·1 kJ mol^{-1}
Zero-point vibrational energy	25·9 kJ mol^{-1}
Rotational energy of H_2	2·5 kJ mol^{-1}
Translational energy of H_2	3·8 kJ mol^{-1}
Correction for PV term	2·1 kJ mol^{-1}
Bond energy of H_2	435·1 kJ mol^{-1}

Two conclusions follow immediately from these figures. In the first place the corrections for rotation and translation and the PV term are small, but that for the zero-point vibration is more significant. In the second place the electronic binding energy is only a small proportion (here about one-seventh) of the total electronic energy. If we had chosen heavier atoms the fraction would have been even smaller. Thus for Li_2 the ratio is 1 in 14 and for methane it is no more than 1 in 38. The binding energy is thus the difference of two much larger quantities, and if we want to calculate it with a reasonable accuracy we must be able to compute these other quantities (electronic energy of the molecule and total electronic energy of the separate atoms) with even more precision. As we shall see, this imposes very severe restrictions on *ab initio* calculations of binding energies, though fortunately it does not affect the main basis of the theory of valence.

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† The thermodynamic internal energy U refers to a bulk sample (e.g. 1 mol) whereas we have been discussing the energy E of a single atom or molecule. For 1 mol of a dilute gas (intermolecular forces negligible) $U = LE$ where L is the Avogadro constant ($6{\cdot}022 \times 10^{23}$ mol^{-1}). The bond energies etc. quoted above are more usually quoted in kJ mol^{-1} (e.g. 916 kJ is the binding energy of $6{\cdot}022 \times 10^{23}$ H_2O molecules, while that for a single molecule is 9·49 eV). Tables of units and conversion factors appear at the end of this book.

There is one interesting corollary which follows from the energy values given above. Since the binding energy is a small difference between larger quantities, we must expect it to be very sensitive to the atoms being bonded. There is, in fact, a specificity about bond energies which is quite absent from most other types of force. This was recognized as long ago as the time of Berzelius, though he could not relate it, as we can do, to subtle differences in electronic behaviour. A few examples will serve to illustrate this specificity.

(*a*) The strongest known single bond in a diatomic molecule is the HF bond whose energy (563·4 kJ mol^{-1}) greatly exceeds that of either HH or FF (432·0 and 154·9 kJ mol^{-1} respectively). Evidently hydrogen and fluorine are mutually adapted to the formation of a strong bond much better than are either of them to bond formation with another atom of the same kind. An explanation of this will be found in Chapter 5.

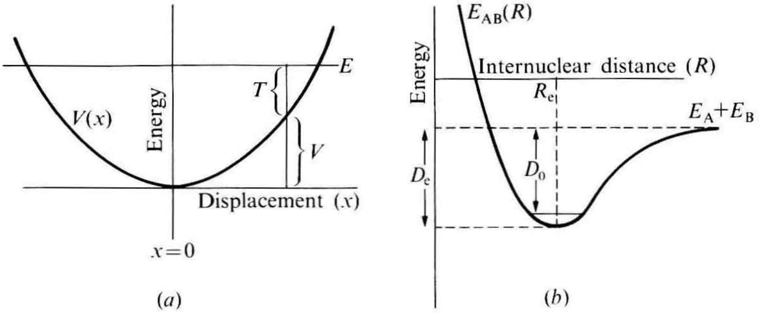
(*b*) Phosphorus and nitrogen show single-bond energies (P—P and N—N) which are not very different ($\sim$200 and 167 kJ mol^{-1}, respectively) and the structure of the atom is much the same in both cases, yet phosphorus forms a stable tetrahedral molecule P_4 and nitrogen does not.

(*c*) The 'inert gas' atoms such as Ne, Xe, Kr,... were long thought to be incapable of forming chemical bonds, but in recent years many stable molecules, such as XeF_2, have been synthesized with bond energies as large as 200 kJ mol^{-1}.

The bonding thus depends on a specific pairing of atoms or on a specific geometry of a compound, rather than on intrinsic properties of the individual atoms. To be wholly successful, a theory must be able to account for all such peculiarities.

1.4. Energy diagrams

Energy relationships in a molecule are often summarized pictorially in an energy diagram. Two such diagrams are shown in Fig. 1.1. The first curve shows the potential energy V of a particle bound to the origin ($x = 0$) by an elastic force proportional to the displacement $F = -kx$. A positive force component means one directed along the positive x axis, and the minus sign thus indicates that the force is towards the origin. The work done by an equal and opposite force in pulling the particle away from the origin to a distance x is thus $\int_0^x kx\,\mathrm{d}x = \frac{1}{2}kx^2$; this is the *potential energy* as a function of x, and $V = V(x) = \frac{1}{2}kx^2$ gives the parabola shown. According to classical mechanics, which turns out to be a good first approximation in dealing with relatively massive particles such as nuclei, the vibrational motion corresponding to a total energy E may be discussed as follows. We draw a horizontal line in the diagram at height E and invoke the result $E = T + V$ (conservation of energy)



(*a*) (*b*)

FIG. 1.1. Energy diagrams: (*a*) particle oscillating about the origin ($x = 0$) with energy E; (*b*) potential energy curve for a diatomic molecule AB showing E_{AB} as a function of internuclear distance R.

in which $T = \frac{1}{2}mv^2$ is the *kinetic energy*. For any value of x (i.e. position of the particle) the two segments of a vertical line (as shown in Fig. 1.1 (*a*)) then indicate the simultaneous values of the kinetic and potential energies. Evidently when the particle passes through the origin $V = 0$ and its energy is wholly kinetic, but as its displacement increases T diminishes to zero, and at the extremities of its motion the particle comes momentarily to rest—its energy then being entirely potential energy. The particle cannot *pass* the points where $T = 0$, because to do so its kinetic energy would have to become negative—which is impossible for any real value of the velocity. The points at which $T = 0$ therefore indicate the extremities of the motion, according to classical physics, and hence the *amplitude* of the vibration. If we give the system more energy, i.e. increase the value of E, the amplitude of the motion increases, but the particle is still confined to a classically 'allowed' region between the points at which the line at height E is intercepted by the potential energy curve. The force acting on the particle is $F = -\mathrm{d}V/\mathrm{d}x$ and therefore vanishes where the potential energy curve has a stationary point; when the stationary point is a *minimum*, as at the origin in Fig. 1.1 (*a*), a particle at rest at that point would be in *stable equilibrium*, any small displacement resulting in a force directed towards restoring the equilibrium. Energy diagrams retain their usefulness in quantum mechanics, with a modified interpretation which we discuss in Chapter 2.

The second diagram, Fig. 1.1 (*b*), shows a potential energy curve for a typical diatomic molecule AB; the quantity plotted is $E_{AB}(R)$, the total electronic energy discussed in §1.4, which plays the part of a potential energy when we are thinking of the motion of the nuclei. When R is very large $E_{AB} \rightarrow E_A + E_B$, the sum of the electronic energies of the separate atoms A and B. As the atoms approach, E_{AB} reaches a minimum at some value $R = R_e$, the equilibrium internuclear distance in the stable molecule AB. At distances less than R_e, the energy curve begins to rise, any bonding effect produced by the electrons

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