NUCLEAR QUADRUPOLE COUPLING AND CHEMICAL BONDING

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RECENTLY the adequacy of modern valence theory has been severely tested by the results provided by the newer spectroscopic techniques including microwave [1-4] and nuclear quadrupole resonance spectroscopy.[5] In some instances, such as the determination of bond lengths and dipole moments of gaseous molecules, a much higher accuracy has been achieved; in the case of nuclear quadrupole coupling constants, however, the information obtained is of a radically new kind.

Nowadays chemical bonds are classified as covalent or ionic; moreover, covalent bonds can have bond-orders of one, two, or three. It is believed that in certain environments a bond can possess a hybrid character, *i.e.*, a bond can embody covalent and ionic character and in addition have a non-integral bond-order.

Modern spectroscopy has provided results of such high accuracy that it is now clear that the properties of a chemical bond, such as a carbon–chlorine bond, vary with its molecular environment. No two carbon–chlorine bonds in differing molecular environments are ever exactly the same; they differ, albeit minutely, in properties such as length or ionic character.

The determination of the electronic distribution in chemical bonds is one of the most important aims of chemical physicists. In general, this is difficult since most bond parameters such as length and moment are connected with the properties of the molecule as a whole. If it were possible to insert a charged probe at different points within a molecule and to measure the forces exerted upon it, or its potential energy, then the charge distribution could be studied. Dailey[6] has pointed out that quadrupolar nuclei act as "built-in" probes, but since their relative position within the molecule is fixed, they give information about the electronic distribution at one point only.

The purpose of this Review is to examine the type of information about

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[1] W. Gordy, W. V. Smith, and R. Tramburulo, "Microwave Spectroscopy", John Wiley and Sons, Inc., New York, 1953.

[2] M. W. P. Strandberg, "Microwave Spectroscopy", Methuen and Co., Ltd., London, 1954.

[3] C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy", McGraw-Hill Book Co., Inc., New York, 1955.

[4] D. J. E. Ingram, "Spectroscopy at Radio and Microwave Frequencies", Butterworths, London, 1955.

[5] H. G. Dehmelt, *Amer. J. Phys.*, 1954, **22**, 110.

[6] B. P. Dailey, *J. Phys. Chem.*, 1953, **57**, 490.

the chemical bond which can be obtained from quadrupole coupling constants. The significance of nuclear quadrupole coupling constants, in relation to the theory of valence, has been emphasised by Townes and Dailey [7] and by Gordy.[8]

Nuclear Quadrupole Coupling.—When the spin, I, of an atomic nucleus is greater than one-half, its distribution of positive charge is non-spherical in shape. With respect to the spin axis the ellipsoid of positive charge can be either prolate or oblate (Fig. 1). In the case of the prolate distribution of charge it can be imagined that some of the positive charge has migrated leading to an excess of positive charge at the North and South poles (represented by positive signs) balanced by a defect of positive charge at the equator (represented by negative signs). The opposite state of affairs occurs with the oblate distribution of charge. The nuclei then possess electric quadrupole moments, Q, which measure the deviation of the nuclear charge from spherical symmetry. In terms of the nuclear dimensions

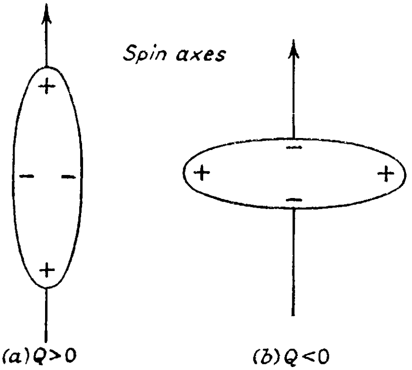

FIG. 1

Nuclear quadrupole moments.

$$Q = \int \rho r^2(3\cos^2\alpha - 1)\,d\tau$$

where ρ is the nuclear charge density, r is the distance from the centre of gravity of the charge to the element of volume $d\tau$, and α is the angle between r and the spin axis. A positive value for Q indicates that the nucleus is elongated along the spin axis (Fig. 1*a*) ; a negative one indicates that it is flattened along this axis (Fig. 1*b*).

In atoms and molecules nuclei are embedded in an electronic cloud. When the electrons and other charges outside a particular quadrupolar nucleus have a non-spherical charge distribution, there is an interaction between the nuclear field and the external field. A nucleus possessing a quadrupole moment situated in an inhomogeneous electric field possesses a potential energy which depends upon the orientation of the quadrupole

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[7] C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, 1949, **17**, 782.

[8] W. Gordy, *Discuss. Faraday Soc.*, 1955, **19**, 14.

moment with respect to the external field. The possible orientations of the spin axis of a nucleus in a molecule, relative to the axis of rotation of the molecule as a whole, are quantised. When the quadrupole moment, Q, interacts with an inhomogeneous electric field of the molecule, each of the allowed orientations of the nucleus may possess a different potential energy. There will, then, be a number of different energy states, which are responsible for the hyperfine structure of rotational lines. This hyperfine structure is resolvable in the microwave region and was first observed by Good[9] in the case of ammonia.

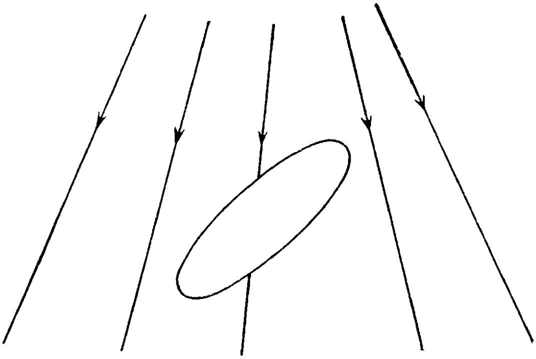

FIG. 2

Quadrupolar nucleus in an inhomogeneous field.

The quadrupole coupling energy of a single nucleus is directly proportional to the quantity eQq, where e is the charge on the proton, Q is the nuclear quadrupole moment, and q, the field gradient, is $\partial^2 V/\partial z^2$, where V is the potential at the nucleus arising from all charges outside the nucleus and z refers to a fixed axis. When the nucleus is situated in an electric charge distribution which is spherically symmetrical, the field gradient, q, is zero. The nuclear quadrupole coupling constant, eQq, can be calculated from the hyperfine structure of rotational lines or from nuclear quadrupole resonance spectra when both Q and q are finite. Effectively q is a measure of the departure from spherical symmetry of the charge distribution at the nucleus due to the electrons and other nuclei present in the same molecule. In those cases[1, 3] where values for Q have been obtained by such methods as atomic beam techniques, the determination of the nuclear quadrupole coupling constant, eQq, enables an accurate value of q to be obtained. This quantity depends on the environment of the quadrupolar nucleus in the molecule, and is therefore intimately connected with the type of valence bonding surrounding the nucleus. In the region near the nucleus, wave-functions which otherwise have proved satisfactory have not previously been tested.

Townes and Dailey argue that since s electrons and filled inner shells have spherical symmetry, and since d and f electrons do not penetrate

[9] W. E. Good, *Phys. Rev.*, 1946, **70**, 213.

sufficiently near the nucleus, the quadrupole coupling constant is largely due to the *p* electrons present in the valence shell. On this basis an insight into the character of chemical bonds can be obtained from the values of quadrupole coupling constants.

Determination of Nuclear Quadrupole Coupling Constants.—The majority of nuclear quadrupole coupling constants, *eQq*, have been obtained from studies of the rotational spectra of polar molecules in the microwave region or by pure quadrupole resonance studies on solids in the radiofrequency region. Coupling constants can also be obtained by molecular beam methods.

Microwave spectroscopy of gases. Cavity oscillators, known as klystrons, generate energy in the microwave region. A simple form of microwave spectroscope (Fig. 3) consists of a klystron, as radiation source, an absorption cell terminated by mica windows, a radiation detector, an amplifier of the detected energy, and an indicator such as a cathode-ray oscilloscope.

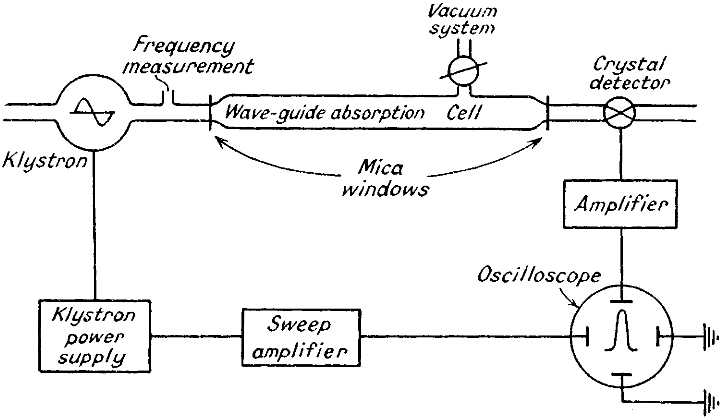

Fig. 3

Block diagram of microwave spectroscope.

A comparison of the apparatus for microwave spectroscopy with that for infrared spectroscopy reveals that the klystron corresponds to the infrared source, a length of rectangular wave-guide to the collimating mirrors, and cell and crystal detector to the thermocouple.

Radiation from a klystron is almost monochromatic. It has a narrow frequency range comparable with that of the absorption bands in the microwave region. Hence during the search for spectral lines the klystron frequency is varied manually. To examine a line in detail, use is made of the fact that the resonant frequency of a klystron tube can be shifted slightly by changing the negative potential on the repeller electrode. By applying the voltage from a saw-tooth generator to this electrode the klystron frequency can thus be swept over a short range. By applying the saw-tooth voltage also to the *X* plates of the oscilloscope, its horizontal sweep becomes proportional to the frequency of the klystron. When the amplified voltage from the detector is applied to the Y plates of the oscilloscope, a continuous and rapid record of the absorption line being studied is reproduced on the oscilloscope screen.

When the rotational spectra of molecules containing a quadrupolar nucleus in an inhomogeneous field are examined with the high resolution afforded by a microwave spectroscope, the rotational levels are found to be split. This hyperfine structure is caused by the coupling of the nuclear spin axis, by means of the quadrupole moment, to the molecular axis of rotation through the electric field gradient, q, effective at the nucleus.

Some twenty years ago Casimir [10] developed the theory of the interaction of nuclear quadrupole moments with surrounding electrons. The energy of interaction E_Q depends on the product of eQq and known functions of the quantum numbers I, J, and K,[11] where J is the rotational quantum number and K the quantum number associated with the component of angular momentum along the symmetry axis z.

The frequencies, in Mc./sec., of the individual lines making up the hyperfine pattern are easily obtained by subtracting the value of the interaction energies, E_Q, of the lower rotational state, J, from those, E_Q', of the upper rotational state, $J + 1$, with the appropriate selection rules, and dividing the result by Planck's constant $\boldsymbol{h}$. For example, for a symmetric-top molecule, the effect of centrifugal distortion being omitted, the frequencies of the hyperfine components would be given by

$$\nu = 2B(J + 1) + (E_Q' - E_Q)/\boldsymbol{h}$$

where $B = \boldsymbol{h}/(8\pi^2 I_b)$, I_b being the moment of inertia about the B axis.

The positive identification of two lines in the hyperfine structure of a rotational transition enables the nuclear quadrupole coupling constant to be calculated. The theoretical and observed hyperfine structure of part of the $J = 7 \rightarrow 8$ rotational transition for the methyl iodide $CH_3 \cdot {}^{127}I$ is shown in Fig. 4.[12]

Hyperfine structure in microwave spectra has been observed and resolved for a number of atoms, including nitrogen, chlorine, bromine, iodine, arsenic, and sulphur. If the quadrupole splittings are not small compared with the rotational frequencies [13] it is necessary to use second-order perturbation theory in order to get the correct energies.[14]

Nuclear quadrupole resonance spectroscopy. In the microwave region the energies associated with the nuclear orientations are observed indirectly as a perturbation of the rotational spectra of molecules in the gas phase. In solids direct transition between levels corresponding to different nuclear orientations can be observed by means of pure nuclear quadrupole spectro-

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[10] H. B. G. Casimir, " On the interaction between atomic nuclei and electrons ", Teyler's Tweede Genootschap, E. F. Bohn, Haarlem, 1936.

[11] A. Nordsieck, *Phys. Rev.*, 1940, **58**, 310 ; B. T. Feld and W. E. Lamb, *ibid.*, 1945, **67**, 15 ; D. K. Coles and W. E. Good, *ibid.*, 1946, **70**, 979 ; J. H. Van Vleck, *ibid.*, 1947, **71**, 468A.

[12] W. J. Orville-Thomas, J. T. Cox, and W. Gordy, *J. Chem. Phys.*, 1954, **22**, 1718.

[13] O. R. Gilliam, H. D. Edwards, and W. Gordy, *Phys. Rev.*, 1948, **73**, 635 ; C. H. Townes, F. R. Merritt, and B. D. Wright, *ibid.*, p. 1334.

[14] J. Bardeen and C. H. Townes, *ibid.*, pp. 627, 1204.

scopy, the frequencies being observed directly in the radiofrequency region. The first observations of nuclear quadrupole resonance spectra were made in 1949 by Dehmelt and Krüger,[15] and numerous investigations have since been made.[1, 4, 5, 16, 17]

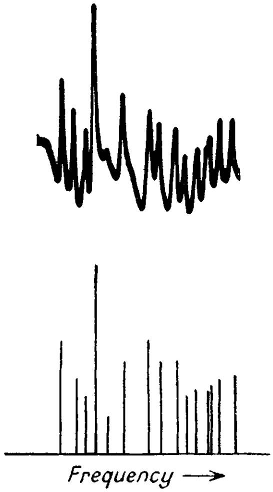

FIG. 4

Theoretical and observed hyperfine lines of the $J = 7 \rightarrow 8$ *transition of* $CH_3 \cdot {}^{127}I$ *at 2·5 mm. wavelength.*

The spectrometers used for detecting pure nuclear quadrupole resonance are very similar to those used for nuclear magnetic resonance except that no magnet is necessary, the external magnetic field being replaced by the internal crystal field of the specimen. Generally a radiofrequency bridge or a type of regenerative oscillator is employed.[18] Radiofrequency power, from a signal generator, is fed into two almost identical resonating circuits which are balanced against each other in a bridge circuit (Fig. 5), the sample

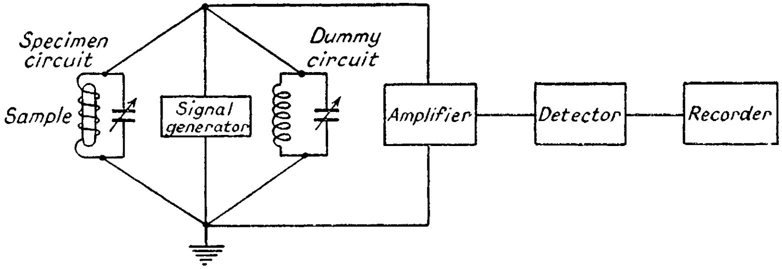

FIG. 5

Block diagram of pure nuclear quadrupole resonance spectroscope.

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[15] H. G. Dehmelt and H. Krüger, *Naturwiss.*, 1950, **37**, 111.

[16] R. Livingston, *J. Chem. Phys.*, 1952, **20**, 496.

[17] M. Davies and W. J. Orville-Thomas, *Ann. Reports*, 1954, **51**, 7.

[18] R. Livingston, *Ann. New York Acad. Sci.*, 1952, **55**, 800; *Phys. Rev.*, 1951, **82**, 289.

being placed in a coil forming the inductive component of the specimen circuit. The resultant output of the two tuned circuits is fed into an amplifier and the detected signal displayed on an oscilloscope or fed into a recorder. As the frequency of the input power is varied a signal is passed on to the detecting system when the specimen absorbs radiofrequency energy and so causes the bridge to become unbalanced. These resonant frequencies can then be measured very accurately.

Nuclear quadrupole resonance spectra are obtained for solids as a result of the interaction between the nuclear quadrupole moment and the *static* crystalline field. In liquids and in gases, on account of the rapid movements of the particles, the gradient at the nucleus varies rapidly and its average value is zero; hence no pure quadrupole spectra are obtained for them.

Nuclear quadrupole resonance spectra have been obtained for a number of molecules containing the following nuclei, ^{10}B, ^{11}B, ^{14}N, ^{33}S, ^{37}Cl, ^{63}Cu, ^{65}Cu, ^{69}Ga, ^{71}Ga, ^{75}As, ^{79}Br, ^{81}Br, ^{121}Sb, ^{123}Sn, ^{127}I, ^{129}I, ^{201}Hg, and ^{209}Bi.

The absorption frequencies are given by the product of eQq and a function of I and M_I, the component of the nuclear spin, I, along the axis of the crystalline field. For a nucleus such as chlorine, with $I = 3/2$, there are two energy levels corresponding to the values of $M_I \pm 3/2$ and $\pm \frac{1}{2}$. There is only one transition frequency for each chlorine isotope:

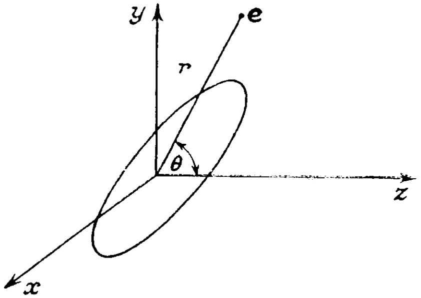
$$\nu = | eQq | (\tfrac{1}{2})$$

The frequencies of these transitions in chlorine compounds have been determined by Livingston.[18] The ratio of the frequencies for the isotopic species ^{35}Cl and ^{37}Cl gives the very accurate value of 1·26878 ± 0·00015 for the ratio $Q(\text{Cl}^{35}) : Q(\text{Cl}^{37})$.

Nuclear Quadrupole Coupling in Atoms.—Before discussing how coupling constants can be interpreted to give information about molecular structure we shall see what factors determine the field gradient at a nucleus. The simpler atomic case will be dealt with first.

Most electrons in atoms are arranged in groups of closed shells. The charge distribution of such shells is spherically symmetric, and produces zero average field at the nucleus. (In effect q, the field gradient, at the nucleus due to the closed shells is zero.) Atoms may possess, in addition to these closed shells, a number of valence electrons.

Let us consider an atom containing one valence electron of charge e.



The potential V at the nucleus due to the electron is

$$V = e/r = e/\sqrt{(x^2 + y^2 + z^2)}$$

where r is the distance from the nucleus to the electron whose co-ordinates are x, y, z. We have then

$$\partial^2 V/\partial z^2 = e(3z^2 - r^2)/r^5 = e(3\cos^2\theta - 1)/r^3$$

since $z = r\cos\theta$ and θ is the angle between the fixed z axis and the radius vector r. When this quantity is averaged over the orbital occupied by the electron, we obtain the contribution of the valence electron to q, the potential gradient at the nucleus, *viz.*,

$$q = e\int \phi\left(\frac{3\cos^2\theta - 1}{r^3}\right)\phi^*\,d\tau \quad . \quad . \quad . \quad (1)$$

where ϕ is the wave-function for the electron. If the electron is in a central field ϕ is separable into a radial factor and a function depending upon the angles. On integration, eqn. (1) yields

$$q = -[2le/(2le + 3)](1/r^3)_{\text{av.}} \quad . \quad . \quad . \quad (2)$$

where l is the orbital angular momentum of the electron and $(1/r^3)_{\text{av.}}$ is the average value of the inverse third power of the distance between the electron and the nucleus.

In the case of atoms the field gradient q can often be calculated from experimental data because measurable quantities such as the nuclear magnetic hyperfine structure [19] and the fine-structure splitting of atomic spectra [20, 21] depend upon $\int \phi(1/r^3)\phi^*\,d\tau$.

For atoms of known quadrupole moment, Q, the field gradient at the nucleus can be determined from the value of the atomic coupling constant, eQq (atom).[22] These experimental values differ by some 10% from the calculated q values. In deriving the expressions connecting q with fine-structure splittings or with magnetic hyperfine structure it has been assumed that the closed shells of electrons are spherically symmetrical. The inner shells are, however, polarised by the valence electron and as a result the electrons in the inner shells tend to keep as far as possible from the position of the valence electron. This polarisation effect produces at the nucleus a contribution to q which is opposite in sign to that attributable to the valence electron. Thus inner shells to some extent shield the nucleus from fields due to the valence electrons. When there is more than one valence electron the problem is more difficult and only a less exact evaluation of q is possible.[10]

In many cases no fine-structure splitting or nuclear magnetic hyperfine structure data are available. However, approximate values of the field

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[19] R. G. Barnes and W. V. Smith, *Phys. Rev.*, 1954, **93**, 95.

[20] R. Bacher and S. Goudsmit, " Atomic Energy States ", McGraw-Hill Book Co., New York, 1932 ; C. E. Moore, Atomic Energy Levels, National Bureau of Standards, Circular 467, U.S. Government Printing Office, Washington, D.C., 1949.

[21] H. A. Bethe and R. F. Bacher, *Rev. Mod. Phys.*, 1936, **8**, 226.

[22] L. Davis, B. T. Feld, C. W. Zabel, and J. R. Zacharias. *Phys. Rev.*, 1948, **73**, 525.

gradient q can be obtained by substituting hydrogen-like electronic wave functions in eqn. (1). By this method Townes and Dailey [7] computed the relative value of q for various atomic states n, l, $m = 0$ (where n, l, and m are the usual electronic quantum numbers). Their results show that with increasing n there is a steady decrease in the value of q and a similar effect occurs when the value of l increases. The effect of changing l, however, is much more marked owing to a correspondingly larger change in screening. Even in the lighter elements fluorine and sodium, where screening effects are less important, the field gradient at the nucleus decreases rapidly with increasing n or l.

Atomic-beam experiments lead to values for the nuclear quadrupole coupling constants, eQq, in atoms. These values vary widely: for ^{35}Cl, ^{79}Br, and ^{127}I, eQq is $-$ 109·74, + 769·62, and $-$ 2292·439 Mc./sec. respectively.

Nuclear Quadrupole Coupling in Molecules.—The calculation of the field gradient at a particular nucleus within a molecule is a complex task. An explicit solution of the problem would entail an intimate knowledge of the distribution of charges in the molecule. The contribution from each nucleus and electron would have to be summed to give the correct resultant field gradient at a specific nucleus. Essentially this entails a determination of wave-functions for the electrons since the effect of adjacent nuclei on the field gradient at a particular nucleus is small. An explicit solution to this problem with use of an accurate wave-function has been achieved only for the hydrogen molecule.[23] White [24] and Bassompierre [25] have recently attempted to calculate q at the deuterium atom in DCN and at the nitrogen atom in HCN respectively, and calculations of this type will undoubtedly become more accurate and be of great value in the future.

Theoretical estimates of various molecular parameters such as bond-order and dipole moment have been obtained by the use of approximate wave-functions. In a similar fashion useful information about the field gradient can be obtained since q depends, to a large extent, on a small number of parameters appertaining to bond structure.

If we consider a molecule containing several electrons, the contribution to Q of the i-th electron is

$$q_i = e \int \psi_i \left(\frac{3 \cos^2 \phi - 1}{r^3} \right) \psi^* \, d\tau \quad . \quad . \quad . \quad (3)$$

where ψ_i is the wave-function for the orbital of this electron *in the molecule*. Approximate solutions for the molecular case can be obtained by assuming that the molecular orbitals, ψ_i, can be replaced by atomic orbitals, ϕ_i, for the atoms in molecules. This approximation was introduced by Townes [26] and developed in a classic paper by Townes and Dailey; [7] the theory has been used with reasonable success in a number of instances.[3, 27, 28]

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[23] A. Nordsieck, *Phys. Rev.*, 1940, **58,** 310.
[24] R. L. White, *J. Chem. Phys.*, 1955, **23,** 253.
[25] A. Bassompierre, *Discuss. Faraday Soc.*, 1955, **19,** 260.
[26] C. H. Townes, *Phys. Rev.*, 1947, **71,** 909.
[27] W. Gordy, H. Ring, and A. B. Burg, *ibid.*, 1950, **78,** 512.
[28] C. C. Loomis and M. W. P. Strandberg, *ibid.*, 1951, **81,** 798.

In their analysis Townes and Dailey showed that the magnitude of the field gradient at a nucleus depends very largely on how the p-type orbitals of lowest energy are occupied by the valence electrons associated with the nucleus. The main contributions to $q \equiv \partial^2 V/\partial z^2$ at a particular nucleus A in a molecule arise from (*a*) valence electrons associated with the chemical bonding in the molecule and having a high probability of being near nucleus A ; (*b*) lone-pair electrons associated with nucleus A ; (*c*) the electrons and nuclei present in the rest of the molecule (these are essentially at distances of more than an atomic radius from nucleus A) ; and (*d*) polarisation of the inner closed shells of electrons which surround nucleus A.

At first sight it seems that contributions of type (*c*) are the only extra feature in the molecular as compared with the atomic case, but since the wave-functions of the valence electrons of an atom in a molecule are very much changed by the formation of chemical bonds, in effect contributions of types (*a*) and (*b*) are modified to some extent from the relatively simple atomic case.

(*a*) *and* (*b*). *Contributions of electrons in the valence shell.* Townes and Dailey [7] estimated the contributions of valence electrons to the field gradient at a nucleus by expressing the wave-function of a valence electron forming part of a covalent bond as an expansion in terms of atomic wave-functions,

$$\psi = \Sigma\, a_i \phi_i \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Usually the coefficients of the lowest-energy atomic orbitals are expected to have the greatest values in the molecular wave-function of the valence electron, *i.e.*, a_i will be largest for the lowest allowed values of n and l.

Substitution of eqn. (4) in eqn. (3) gives an expression which represents the contribution of the valence electron to q. An estimate of the magnitude of each term in this expression has been obtained by Townes and Dailey who showed that the dominating term will be the state of lowest allowed total quantum number n,

$$i.e., \quad q \text{ (Valence electron)} \approx e a_i^2 \int \phi \left(\frac{3\cos^2\theta - 1}{r^3} \right) \phi^* \, d\tau = |\, a_i \,|^2 q_i$$

where q_i represents the field gradient arising from an electron whose atomic wave-function is ϕ_i. This is reasonable since energy considerations will ensure that the fractional importance $|\, a_i \,|^2$ of this atomic state will be large, and in addition the value of the field gradient for this state of lowest allowed energy is considerably larger than those for the higher-energy atomic states.

(*c*). *Contributions due to the other charges present in the molecule.* The approximate effects of other charges present in the molecule on the magnitude of the field gradient at a nucleus can be calculated in a simple fashion. If, for example, we assume that a neighbouring ion at a distance of 2 Å from the nucleus has an average charge of $e/2$ then it produces a value of $q = 6 \times 10^{13}$ e.s.u. at the nucleus ; a charge of e placed 1 Å from the nucleus contributes $9{\cdot}6 \times 10^{14}$ e.s.u. to q. These contributions are small compared with the contribution of a valence electron in a low energy p state and so may be neglected.

(*d*). *Polarisation effects on the inner shells.* In the last section it was seen that a neighbouring ion makes only a small contribution to the field gradient at a nucleus. In addition to this direct effect a neighbouring ion will distort the electronic distribution about a nucleus. This polarisation of the inner shells will contribute to q. This problem has been analysed by Townes and Dailey who showed that the contributions to q from the polarisation of a particular shell amounted to less than 1% of the value due to a single electron *of this shell.* The indications are that such distortions could increase the contribution to q of a neighbouring ion by a factor of ten. If, as in the preceding section, we have an ion of average charge $e/2$ at a distance of 2 Å from the quadrupolar nucleus, then its contribution to q could be increased by polarisation effects to 6×10^{14} e.s.u. This is still a rather small contribution amounting to less than 2% of the value of the field gradient due to a single valence p-electron in iodine. Hence contributions to the field gradient at a nucleus due to neighbouring ions or to polarisation effects can frequently be neglected.

This analysis of the importance of the various contributions indicates that if the lowest-energy atomic state is a p state the field gradient at a nucleus due to a single valence electron is (to a first approximation) $q = |\, a_p \,|^2 q_p$, where $|\, a_p \,|^2$ is the importance of the p wave-function in the molecular wave-function, and q_p represents the value of the field gradient for a p atomic state.

Overlap and Nuclear Quadrupole Coupling.—If ψ represents the molecular wave-function of a bonding electron its contribution to the field gradient at a nucleus A is given by eqn. (3). If A is joined to B by a chemical bond the electron will be in a molecular orbital whose wave-function can be expressed as

$$\psi = a\phi(\mathrm{A}) + b/\phi(\mathrm{B})$$

Qualitatively we can divide the electronic density of the bond into three parts. The electronic density near the nucleus A, which depends on the importance of the atomic orbital $\phi(\mathrm{A})$ in the molecular orbital ψ, will provide the dominant contribution to the field gradient at A. A second contribution to q arises from the charge cloud in the overlap region. This cloud is approximately the distance of one covalent radius away from the nucleus A, and because of the inverse variation with r makes only a small contribution to q. The electronic density of the bonding electrons near nucleus B will affect the field gradient at A even less.

The effect of overlap on the field gradient at a nucleus can be calculated [29–31] by conventional means (by use of the overlap integral normally used in theoretical chemistry); this procedure has been shown [32] to underestimate the field gradient due to the bonding electrons. This application of molecular-orbital theory is incorrect since it implies that when the covalent bond is formed an appreciable amount of charge density is removed from regions close to the nucleus, but as this would need considerable energy

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[29] P. Shatz, *J. Chem. Phys.*, 1954, **22**, 695.

[30] *Idem, ibid.*, p. 755.

[31] *Idem, ibid.*, p. 1974.

[32] W. Gordy, *ibid.*, p. 1470.

it seems improbable.[1] Gordy has pointed out that the charge cloud concentrated in the overlap region can be formed with the expenditure of less energy by a redistribution of the charge cloud in the outer parts of the atomic orbitals. These outer distortions would be expected to have only a small influence on the field gradient at the nucleus because of the inverse-cube variation of q with r. These qualitative considerations and some experimental data on quadrupole coupling in halogens seem to indicate that near the nucleus the electronic charge of a homopolar bond can be divided equally between the two atoms, so that, on the average, there is one electron in each of the atomic orbitals $\phi(\mathrm{A})$ and $\phi(\mathrm{B})$. This is equivalent to putting the overlap integral equal to zero when we are concerned with the calculation of quadrupole coupling. It seems then that the molecular wave-functions hitherto found satisfactory for calculating the properties of valence bonds are not appropriate for the calculation of field gradients *near the nuclei.*

Ionic Character and Hybridisation.—Two other factors that affect the electronic distribution near a nucleus in a molecule, in particular its p-character (as compared with an atom), are (*a*) the degree of ionic character of the bond and (*b*) the degree of hybridisation of the bond-forming orbital.

(*a*) *Ionic character.* The effect of ionic character on q can be seen as follows, by considering the simple case of a diatomic molecule such as thallous chloride, TlCl. The electronic configurations of the ground states of the two atoms are Tl (. . . $6s^2 6p$), Cl (. . . $3s^2 3p^5$). It might be assumed that TlCl possesses a σ bond formed by using a p orbital of each atom. If we consider the bond to be homopolar there is, on the average, one electron each in the orbitals $\phi(\mathrm{Tl}{:}6p)$ and $\phi(\mathrm{Cl}{:}3p)$. In these circumstances the thallium nucleus is surrounded by filled electronic shells plus a single *extra* electron in the Tl:$6p$ orbital : similarly the chlorine nucleus is surrounded by filled shells with the exception of the valence shell which has a *defect* of one Cl:$3p$ electron. Filled inner shells have spherical symmetry and do not contribute to q ; hence the field gradient at the thallium nucleus arises from a single electron in the $6p$ orbital, *i.e.*, $q_{\mathrm{Mol.}} = q_p^{\mathrm{Tl}}$. For the chlorine nucleus $q_{\mathrm{Mol.}} = -\, q_p^{\mathrm{Cl}}$, the negative sign indicating a defect of one $3p$ electron from a closed-shell configuration.

On the other hand, if the atoms are held by an ionic bond, $\mathrm{Tl^+Cl^-}$, the field gradients at the nuclei will be zero, since apart from polarisation effects the charge distribution is spherical. If the ionic structure $\mathrm{Tl^+Cl^-}$ has a fractional importance x the importance of the covalent structure Tl–Cl will be $(1 - x)$. Each structure will contribute to q an amount given by the product of its fractional importance and the value of q for the bond structure concerned.

Hence for thallium, $$q_{\mathrm{Mol.}} = (1 - x)q_p^{\mathrm{Tl}} + xq^{\mathrm{Tl}^+}$$

or $$eQq^{\mathrm{Tl}}_{\mathrm{Mol.}} = (1 - x)eQq_p^{\mathrm{Tl}} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where eQq_p is the nuclear quadrupole coupling constant arising from one valence p electron. This quantity is related to the coupling constant measured for atoms by atomic-beam techniques.

Similarly for the chlorine nucleus,

$$eQq^{\mathrm{Cl}}{}_{\mathrm{Mol.}} = -(1-x)eQq_p{}^{\mathrm{Cl}} \quad . \quad . \quad . \quad . \quad (6)$$

where $eQq^{\mathrm{Tl}}{}_{\mathrm{Mol.}}$ and $eQq^{\mathrm{Cl}}{}_{\mathrm{Mol.}}$ are the experimental values for the nuclear quadrupole coupling constants.

By convention the quantity multiplying $-eQq_p{}^{\mathrm{Tl}}$ or $-eQq_p{}^{\mathrm{Cl}}$ in eqns. (5) and (6) is known as the amount of unbalanced p electrons, U_p, oriented along the bond. The quadrupole coupling constant is then $-U_p$ multiplied by the coupling per p electron, eQq_p, and hence

$$U_p = -eQq_{\mathrm{Mol.}}/eQq_p \quad . \quad . \quad . \quad . \quad (7)$$

In TlCl, $U_p = -(1-x)$ for Tl and $U_p = (1-x)$ for Cl. In the chloride ion, Cl^-, there are a number of p electrons whose effects cancel out. In this case $U_p = 0$.

The quadrupole coupling constants of ^{35}Cl and ^{79}Br in a number of differing molecular environments are given in Table 1. The small values obtained for the coupling constants of the halogen nuclei in potassium chloride and potassium bromide indicate very clearly that these molecules must be essentially ionic. Thallous chloride and lithium bromide must also be essentially ionic. The other molecules listed in Table 1 have bonds to halogen which have a mixed nature. They are primarily covalent in nature but have some ionic character.

TABLE 1. *Quadrupole coupling constants of* ^{35}Cl *and* ^{79}Br *in molecules*

Molecule	eQq (Mc./sec.)	Molecule	eQq (Mc./sec.)
Cl (Atomic) . .	− 109·74 ($-eQq_p$)	^{79}Br (Atomic) .	769·8 ($-eQq_p$)
BrCl	− 103·6	BrCl	876·8
ICI	− 82·5		
$\mathrm{CH_3{\cdot}Cl}$ . . .	− 74·8		
$\mathrm{SiF_3Cl}$ . . .	− 43·0	$\mathrm{SiF_3Br}$	440·0
TlCl	− 15·8		
		LiBr	37·2
KCl	0·041	KBr	10·24

(*b*) *Hybridisation.* Ionic character is not the only factor which tends to lower the value of eQq at a nucleus in a molecule below the value found for the same nucleus in an atom. The experimental data available reveal that the quadrupole coupling constants for chlorine atoms, predominantly covalently bound, lie near − 80 Mc./sec., and are considerably lower than those to be expected if the chlorine atoms used pure p orbitals for bonding. For such pure p bonding the value obtained for $eQq_{\mathrm{Mol.}}$ should approximate to that obtained for atomic chlorine, *viz.*, − 109·74 Mc./sec. A good example is iodine monochloride, ICl, where the small difference of 0·4 unit between the electronegativities [33] of the two atoms leads one to expect only a small amount of ionic character in the bond. Notwithstanding this, the coupling in iodine monochloride is appreciably less than the value obtained for atomic

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[33] W. Gordy and W. J. Orville-Thomas, *J. Chem. Phys.*, 1956, **24**, 439.

chlorine. In these cases it has been assumed that hybridisation of the chlorine atomic orbital used for bonding occurs.

The molecular orbital for a bond A–B has the wave-equation

$$\psi = a\phi(\mathrm{A}) + b\phi(\mathrm{B})$$

If the atomic orbital $\phi(\mathrm{A})$ is hybridised, its wave-function can be written in the form

$$\phi(\mathrm{A}) = \sqrt{s}\phi_s + \sqrt{p}\phi_p + \sqrt{d}\phi_d$$

which implies that the orbital has s character of an amount s and d character of amount d. When a bond possesses ionic character $a \neq b$, and if we define the ionic character, i, of the bond by a well-known convention as $i = a^2 - b^2$, it can be shown that for a covalently bonded halogen atom

$$eQq_{\mathrm{Mol.}} = [1 - s + d - i(1 - s - d)]eQq_p \quad . \quad . \quad (8)$$

If a quantity ρ be defined as

$$\rho = | \, eQq_{\mathrm{Mol.}}/eQq_p \, |$$

eqn. (8) can be arranged to

$$i(1 - s - d) + s - d = 1 - \rho \quad . \quad . \quad . \quad (9)$$

where s and d give a measure of the s and d character of the bonding orbital, $\phi(\mathrm{A})$, of atom A. When $a^2 > b^2$ the coupling atom A carries a negative charge.

If the extent of hybridisation (s and d) and the ionic character i are known then eqn. (9) can be used to calculate ρ. If the quadrupole moment of the nucleus A is known then the value for $eQq_{\mathrm{Mol.}}$ gives a direct estimate of Q, the field gradient at the nucleus A. In practice the amount and type of hybridisation and i are unknown and the procedure is reversed. The experimentally determined values for the nuclear quadrupole coupling constants in molecules are used in an attempt to obtain an insight into the character of the bond, *i.e.*, hybridisation and ionic character. Unfortunately relation (9) contains three unknown quantities, s, d, and i, and only one measurable quantity ρ. By use of quadrupole data alone, then, it is not possible to separate effects due to hybridisation from those due to ionic character. The leading workers in the field agree that the effects of d hybridisation are probably small and can be neglected, *i.e.*, $d = 0$ in eqn. (9). This leaves us with two unknowns and one experimental datum.

In order to overcome this final difficulty attempts have been made to derive a relation between the ionic character of a bond A–B and the electronegativity difference between the atoms A and B. Curves connecting ionic character and electronegativity difference ($X_{\mathrm{A}} - X_{\mathrm{B}}$) have been put forward for bonds to halogen atoms by Gordy [8, 32, 34] and by Dailey and Townes.[35] These curves are used to give an estimate of the ionic character possessed by a bond, which value, when substituted in eqn. (9), enables a value for the hybridisation factor to be obtained.

The curves of Gordy and of Dailey and Townes disagree most markedly

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[34] W. Gordy, *J. Chem. Phys.*, 1951, **19**, 792.

[35] B. P. Dailey and C. H. Townes, *ibid.*, 1955, **23**, 118.

in the region of small ionic character. In this region the quadrupole coupling constants are extremely sensitive to the degree of hybridisation assumed. Gordy points out that for the homopolar molecules Cl_2 and Br_2, $i = 0$ and the observed $\rho = 1$. Substitution of those values in eqn. (9) shows that either $s = d$ or $s = d = 0$. Similarly for crystalline iodine, if a correction is made for cross-bonding,[36] $s \approx d$ to a good approximation. It should be pointed out that these results are obtained from solid-state data and the situation in the vapour phase need not necessarily be the same. Molecules such as KCl and KBr are generally regarded to be completely ionic, *i.e.*, $i = 1$. The experimental values obtained for the quadrupole coupling constants give $\rho \approx 0$. Insertion of these values in eqn. (9) shows that $d = 0$. On this basis Gordy argues that the experimental evidence indicates that hybridisation does not exist either in the pure covalent or in the pure ionic state unless $s \approx d$. Consequently, Gordy reduces eqn. (9) to

$$i = 1 - \rho \quad . \quad . \quad . \quad . \quad . \quad (10)$$

These equations are taken to give a measure of the ionic character of the type that puts the negative pole on the coupling halogen atom. Using relation (10), Gordy has obtained values for the ionic character possessed by bonds to halogen atoms in a number of diatomic and polyatomic molecules. These values (Table 2) are plotted against the corresponding electronegativity differences in Fig. 6. The curve obtained by Gordy levels off at the top for molecules such as those of the alkali-metal halides which are considered to be completely ionic. This curve has led Gordy to propound the approximate rules $i = \frac{1}{2}(X_A - X_B)$ for $| X_A - X_B | < 2$ and $i = 1{\cdot}00$ for $| X_A - X_B | > 2$. Regardless of whether $(1 - \rho)$ represents

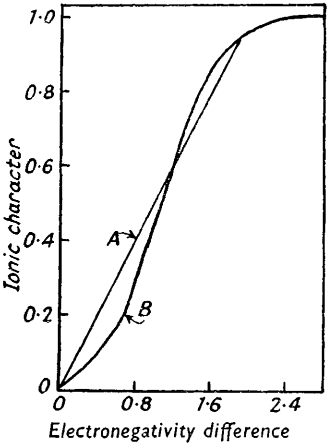

FIG. 6

Plot of ionic character against electronegativity difference.
A, Gordy.[8] *B*, Dailey and Townes.[35]

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[36] H. Robinson, H. G. Dehmelt, and W. Gordy, *J. Chem. Phys.*, 1954, **22**, 511.

the true ionic character of a bond, Fig. 6 shows a systematic variation of the coupling ratio $| eQq_{\text{Mol.}}/eQq_p |$ with electronegativity difference.

Gordy derived relation (10) on the assumption that the atoms use pure *p* atomic orbitals in bond formation. The possibility of small amounts of hybridisation, up to $\sim 3\%$ of *s* or *d* character, or even larger amounts if *s* and *d* hybridisation are approximately equal, cannot, however, be ruled out.

This view of pure *p* bonding by the halogens is not shared by Townes and Dailey[37] who made the first attempt to interpret quadrupole couplings. The quadrupole coupling constants for covalently bonded chlorine are some 25% less than the value for atomic chlorine. Townes and Dailey regard this as good evidence that a Cl *sp*-hybridised atomic orbital is used in bonding. They do not believe that this diminution in *eQq* is due entirely to the ionic character of the bond. In their original paper Townes and Dailey obtained an expression for the nuclear quadrupole coupling constant in a diatomic molecule containing chlorine. This expression is equivalent to

$$eQq_{\text{Mol.}} \approx (-1 + s - d)(1 - i)eQq_p \quad . \quad . \quad . \quad (11)$$

For $I^{35}Cl$, $eQq = -82{\cdot}5$ Mc./sec. From Pauling's curve of ionic character against electronegativity difference[38] Townes and Dailey obtained a value of $i = 0{\cdot}08$. Substitution of these values in eqn. (11), together with the value $eQq_p = +109{\cdot}74$ Mc./sec., gives $(s - d) = 0{\cdot}18$. Hence it is quite impossible to distinguish the effects due to *s* hybridisation from those due to *d* hybridisation. It has usually been assumed that very little *d* hybridisation occurs and *d* is put equal to zero in equations (9) and (11). On this basis Townes and Dailey claim that the chlorine bonding orbital in iodine monochloride and other chlorine compounds is an *s–p* hybrid containing some 18% of *s* character. These estimates have been revised to include bromine and iodine. The latest interpretation is condensed in the following rule :[35] " The halogen bonds are hybridised with 15% of *s* character whenever the halogen is more electronegative by 0·25 unit than the atom to which it is bonded. Otherwise there is no hybridisation."

If *d* hybridisation is ignored, relations (9) and (11) reduce to

$$eQq = (-1 + s)(1 - i)eQq_p \quad . \quad . \quad . \quad (12)$$

Townes and Dailey have used this equation in conjunction with their " hybridisation rule " to obtain the ionic character values given in Table 2 and Fig. 6. This curve was obtained from quadrupole coupling constants obtained for diatomic molecules in the gaseous state.

Townes and Dailey point out that small deviations from the curve of Fig. 6 may occur owing to changes in the effective electronegativity of an atom situated in different molecular environments (cf. ref. 33). The amount of ionic character in a bond is also affected by the internuclear distance and by hybridisation. The relation between ionic character and electronegativity difference is therefore not expected to be precise. Gordy's relation and the S-shaped curve of Dailey and Townes do not differ greatly

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[37] B. P. Dailey, *Discuss. Faraday Soc.*, 1955, **19**, 255.

[38] L. Pauling, " The Nature of the Chemical Bond ", Cornell Univ. Press, Ithaca, 1940.

except in that part of the curve where $|\Delta x| \leqslant 1$. In this region there is a paucity of data ; the only points available are provided by FCl and FBr. The interpretation of the nuclear quadrupole couplings in these molecules is complicated since the chlorine and bromine atoms are positively charged.

If the coupling halogen atom carries a positive charge the bond is positively ionic. When the bond is completely ionised to A^+B^-, two electrons are missing from the valence shell of the halogen atom A. The nuclear quadrupole coupling constant arises from a defect of two p electrons in an otherwise spherical shell and $eQq = -2eQq_p$. Since the interaction between a p valence electron and the nucleus is larger when the atom is positively charged, Dailey and Townes[35] introduce a correction factor c such that

TABLE 2. *Ionic character of diatomic halides*

Molecule	eQq (Mc./sec.) (obs.)	s-Character assumed (%)	Ionic character	$1 - \rho$ Gordy
		Dailey and Townes		
^{35}Cl ($-eQq_p$)	− 109·74			
BrCl	− 103·6	0·0	0·06	0·06
ICl	− 82·5	15·0	0·12	0·25
TlCl	− 15·8	15·0	0·83	0·99
KCl	0·04	15·0	1·00	1·00
RbCl	0·774	15·0	0·99	0·99
CsCl	3	15·0	0·97	0·97
FCl	− 146·0	0·0	0·26	—
HCl	—	15·0	0·29	0·40
^{79}Br ($-eQq_p$)	769·76			
BrCl	876·8	0·0	0·110	—
LiBr	37·2	15·0	0·944	0·952
NaBr	58	15·0	0·911	0·925
KBr	10·244	15·0	0·985	0·987
DBr	533	15·0	0·186	0·308
FBr	1089	0·0	0·329	—
^{127}I ($-eQq_p$)	− 2292·84			
DI	− 1823	15·0	0·065	0·205
LiI	− 198·15	15·0	0·900	0·914
NaI	− 259·87	15·0	0·867	0·887
KI	− 60	15·0	0·970	0·974

$$eQq = -2(1 + c)eQq_p$$

When a bond possesses some positive ionic character, eqn. (12) is modified to

$$eQq = [(-1 + s - d)(1 - i) - 2(1 + c)i]eQq_p$$

For the halogens $c \approx 0{\cdot}15$. This equation was used to obtain the values of i for FCl and FBr given in Table 2 and plotted in Fig. 6.

Dailey and Townes attempt to justify their postulation of a comparatively large amount of hybridisation in covalently bonded halogen atoms (when $\Delta x \geqslant 0{\cdot}25$) by pointing out that (i) bond energies of molecules containing elements of the first two rows of the Periodic Table have shown the presence of s hybridisation ; (ii) quadrupole coupling data for compounds of the Group V elements indicate quite strongly the presence of s hybridisation in the bonding orbitals ; (iii) quadrupole coupling data demonstrate unequivocally that certain sulphur bonds are hybridised ; (iv) polyatomic molecules for which coupling constants are known appear to fit the S-shaped curve reasonably well, provided multiple-bonding and bond-interaction effects are allowed for.

To some extent Gordy's belief in the absence of hybridisation in halogen compounds is based on the values obtained for the quadrupole coupling constants of Cl_2, Br_2, and I_2 in the solid state. Gordy makes the assumption that since these are homopolar molecules the coupling constants for the isolated gas molecules will not be far different from the solid-state values. This seems a very reasonable assumption but it is open to criticism.[35]

In the interpretation of the coupling constants obtained for the alkali metal halides the values obtained for the ionic character, being almost unity, are insensitive to the assumption or otherwise of *s* hybridisation. For these molecules Dailey and Townes, in accordance with their " rule ", assume 15% of *s* hybridisation. On simple chemical grounds it seems unnecessary to invoke hybridisation to explain the properties of these molecules which are, as in the case of potassium chloride, completely ionic. Gordy, in his treatment, interprets the coupling constants of these molecules as indicating the absence of hybridisation.

The molecules BrCl and ICl are extremely important to the problem under discussion since the quadrupole coupling constants have been measured for both nuclei in these molecules. Quite clearly the amount of ionic character in the bond should be independent of which coupling constant is used for its estimation. No *s* hybridisation is assumed to be present in BrCl by Gordy or by Dailey and Townes. In this molecule the coupling in the bromine atom indicates 10% of ionic character, and that in the chlorine atom indicates only 6%. The discrepancy here is small and could be caused by a small amount of *d* hybridisation. The ionic character of iodine chloride is found by Gordy to be 23% when the coupling in the chlorine atom is used and 24% with the coupling in the iodine atom. Dailey and Townes, assuming 15% of *s* hybridisation of the chlorine bonding orbital, obtain values of 12% and 24%. The postulation of *s* hybridisation in this case makes the agreement worse.

The Electronic Structure of Polyatomic Molecules.—In terms of valence-bond language the mesomeric state of a molecule can be expressed as a combination of unperturbed structures. Estimates of the fractional importance of the contributing structures can be obtained from bond-length and dipole-moment data. These estimates can be refined by the use of nuclear quadrupole coupling constants. In the following sections it will be shown how the coupling constants to be expected for various combinations of resonating structures can be calculated. By comparing these " theoretical " values with the coupling constant found experimentally, for the molecule concerned, the combination of structures most in accord with all the available data can be chosen.

Symmetric molecules. We have seen in previous sections that the main contribution to the field gradient, *q*, comes from the " unbalanced " *p* electrons in the valence shell of an atom. In practice this is the condition encountered most frequently.

Let us consider chemical elements which have in their valence shells s and p electrons only. If the bond A–B is aligned along the z axis it can be shown that

$$eQq_{\text{Mol.}}{}^{\text{A}} = [-(N_x + N_y)/2 + N_z]eQq_p{}^{\text{A}} \qquad . \quad . \quad (13)$$

where N_x, N_y, and N_z represent the effective electron populations of the p_x, p_y, and p_z orbitals of atom A.

A comparison of eqns. (7) and (13) shows that

$$U_p = (N_x + N_y)/2 - N_z = eQq_{\text{Mol.}}/(-eQq_p)$$

In certain cases the atomic couplings have been accurately determined and values for eQq_p are known (Table 4). A large number of determinations of quadrupole couplings in molecules have also been obtained. Hence for certain compounds, such as the halides, U_p is known experimentally. When the bond A–B possesses some ionic character and the bonding orbital of A is hybridised the number of unbalanced p electrons along the bond is given by

$$N_z = (1 \pm i)(1 + s - d)$$

The positive sign is used for i when the bond has polarity in the sense A^-B^+ and the minus sign when the polarity has the reverse sense. If the change in nuclear screening caused by the formal charges on A and B is taken into account, for an atom like Cl bonded to a less electronegative element the relation becomes,

$$N_z = (1 + i)(1 + c)(1 + s - d)$$

where c is the correction factor for the change in screening caused by the charges on A^- and B^+. A table of values for c has been given by Townes and Schawlow [3] who state that each stage of ionisation modifies the field gradient q by a factor $(1 + c)$; c is 0·15 for the halogens, arsenic, and antimony, 0·20 for oxygen and sulphur, and 0·30 for nitrogen. Positive ionisation, A^+B^-, increases q by pulling all the electrons closer to the nucleus, and negative ionisation, A^-B^+, decreases q. The field gradient for A in the structure A^+B^- is then $q(1 + c)$ and in the structure A^-B^+ it is $q/(1 + c)$ where q refers to the neutral atom.

The number of unbalanced p electrons, U_p, for various types of bond are given in Table 5. When the structure of a bond is intermediate between two or more of the types listed, the resultant U_p (hybrid bond) is obtained by summing the product of U_p multiplied by the fractional importance for each type contributing to the mixed character of the bond.

For example, consider a chemical bond which can be described as a resonance hybrid of the two structures A:B and A^-B^+. If the bond, A–B, has an ionic character i the fractional importances of the covalent and ionic structures are $(1 - i)$ and i respectively. Hence the net unbalanced p electrons is:

$$\begin{aligned} U_p \text{ (Effective)} &= (1 - i)(1 - s + d) + i(0) \\ &= (1 - i)(1 - s + d) \end{aligned}$$

TABLE 3. U_p *for various types of bond.* (*After Townes and Schawlow* [3])

Structure	Electron configuration of A	Bonding orbital used by A	Type of bond	N_x	N_y	N_z	U_p
A:B	s^2p^5 (like Cl)	Pure p	Single covalent	2	2	1	1
A:B	s^2p^5	spd Hybrid	Single covalent	2	2	$1 + s - d$	$1 - s + d$
A^-B^+ . . .	s^2p^6 (like Cl^-)	—	Single ionic	$2/(1 + c)$	$2/(1 + c)$	$2/(1 + c)$	0
A^+B^- . . .	s^2p^4 (like Cl^+)	—	Single ionic	$2(1 + c)$	$2(1 + c)$	0	$2(1 + c)$
A^+B^- . . .		sp Hybrid	Single ionic	$2(1 + c)$	$2(1 + c)$	$2s(1 + c)$	$2(1 - s)(1 + c)$
A=B	s^2p^4 (like O)	σ Bond ; spd hybrid π Bond ; Pure p	Double Covalent	2	1	$1 + s - d$	$\frac{1}{2} - s + d$
A≡B	s^2p^3 (like N)	σ Bond ; spd hybrid π Bond ; Pure p	Triple Covalent	1	1	$1 + s - d$	$- s + d$

Similarly, if a bond possesses ionic character in the opposite sense, *i.e.*, the contributing structures are A·B and A^+B^-, where A uses *sp* hybrid orbitals, then

$$U_p \text{ (Effective)} = (1 - i)(1 - s) + i[2(1 - s)(1 + c)]$$
$$= (1 - s)[1 + i(1 + 2c)]$$

Townes and Dailey [7] and Townes and Schawlow [3] have estimated the percentage importance of the various valence-bond structures contributing to a molecule from bond-length and bond-angle data, modified by consideration of molecular dipole moments and quadrupole couplings. By this means a combination of resonating structures is chosen which gives a value of U_p which is near the observed value obtained by using eqn. (7). In these interpretations it is assumed that the contributions to the field gradient from *p*-type wave-functions will be so predominant that the *d*-orbital contributions can be neglected. The chosen combination is not, of course, unique. An attempt is made to choose a combination which is reasonably in accord with all the experimental data. This procedure can only be applied when the quadrupole coupling constant produced by an excess of one *p* electron along the axis of the bond, *i.e.*, eQq_p, is known. Table 4 gives values for eQq_p for various isotopes. Some of these have been obtained from measurements of atomic spectra whilst others have been estimated from observed coupling constants in a variety of molecules.

In Table 5 some examples are listed of the bond structures and the expected values of U_p derived for certain molecules. The observed values for U_p are included for comparison.

Asymmetric molecules. When the hyperfine structure of the rotational spectra of linear and symmetric-top molecules are analysed only one coupling constant, eQq, is obtained. For an asymmetric rotor or for the quadrupole spectra of solids two independent coupling constants are needed in the analysis of the spectra. These can be expressed as eQq_{zz} and $\varepsilon = (q_{xx} - q_{yy})/q_{zz}$ where $q_{xx} = \partial^2 V/\partial x^2$, $q_{yy} = \partial^2 V/\partial y^2$, and $q_{zz} = \partial^2 V/\partial z^2$ The quadrupole coupling constants are obtained experimentally with reference to the principal axes of the molecule, *a*, *b*, and *c*. These coupling constants can then be resolved along a new set of reference axes, *x*, *y*, *z*, with, for example, the *z*-axis along a chemical bond, by a rotation of axes.[39]

By comparison with eqn. (13) we can define the nuclear coupling with reference to the new axes *x*, *y*, and *z* :

$$eQq_{xx} = -[(N_y + N_z)/2 - N_x]eQq_p$$
$$eQq_{yy} = -[(N_x + N_z)/2 - N_y]eQq_p$$
$$eQq_{zz} = -[(N_x + N_y)/2 - N_z]eQq_p$$

Using these relations, we obtain the asymmetry parameter

$$\varepsilon = \frac{q_{xx} - q_{yy}}{q_{zz}} = \frac{3(N_y - N_x)}{N_x + N_y - 2N_z} \quad . \quad . \quad . \quad (14)$$

The asymmetry parameter, ε, can be obtained from the measured quantities $\partial^2 V/\partial a^2$, $\partial^2 V/\partial b^2$, $\partial^2 V/\partial c^2$, where *a*, *b*, and *c* are the principal axes of the

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[39] J. K. Bragg, *Phys. Rev.*, 1948, **74**, 533.

molecule. This value of ε can be compared with the quantity on the right-hand side of eqn. (14), with assumed values for N_x, N_y, and N_z. In this manner, supplementary information about the way the valence orbitals are filled is obtained.

Goldstein and Bragg [40] have used the asymmetry parameter to show that the C–Cl bond in CH_2:CFCl has only about 5% of double-bond character, and not 15% as had previously been surmised.[41] This method of obtaining an estimate of the double-bond character of conjugated C–Cl bonds has been developed by Bersohn.[42]

The quadrupole coupling of the ^{33}S nucleus in hydrogen sulphide has a large asymmetry parameter [43] of $\varepsilon = -0{\cdot}60$. For a long time it has been supposed that because the inter-bond angle in hydrogen sulphide is approximately 90° the sulphur bond-forming orbitals are nearly pure *p* in character. The large asymmetry parameter obtained for this molecule demonstrates unequivocally that this view is wrong. Gordy [44] has discussed the bonding in hydrogen sulphide in terms of the " multiple bond " molecular-orbital model and has reconciled the observed bond angle with an *s* character for the two bonds of 7%. This is almost twice the value expected from the inter-bond angle of 92°. Similarly in arsine the observed coupling indicates that the arsenic bonding orbitals must have about 9% of *s* character as compared with a value of 4% obtained from a consideration of the inter-bond angle.[44]

TABLE 4. *Quadrupole coupling constants for various nuclei due to one valence* p *electron.* (*After Townes and Schawlow* [3])

Nucleus	eQq_p (Mc./sec.)	Nucleus	eQq_p (Mc./sec.)	Nucleus	eQq_p (Mc./sec.)
^{10}B . . .	− 10·9	^{35}Cl . .	109·7	^{113}In . .	− 886·2
^{11}B . . .	5·3	^{36}Cl . .	23·2	^{115}In . .	− 899·1
^{14}N . . .	− 10 to − 24	^{37}Cl . .	86·4	^{121}Sb . .	2000
^{17}O . . .	3·3	^{75}As . .	600	^{123}Sb . .	2500
^{27}Al . .	− 37·5	^{79}Se . .	− 1400	^{127}I . .	2292·8
^{33}S . . .	55	^{79}Br . .	− 769·8	^{129}I . .	1688
^{35}S . . .	− 39	^{81}Br . .	− 643·1	^{201}Hg . .	− 1000

Quadrupole Coupling in the Solid State.—Pure quadrupole coupling data in solids can be obtained for much more complex molecules than can be investigated in the gaseous state. The interpretation of the coupling data obtained from direct quadrupole spectra of crystalline substances is, however, complicated by the presence of solid-state effects. These effects are added to the uncertainties of not knowing the exact contributions to chemical

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[40] J. H. Goldstein and J. K. Bragg, *Phys. Rev.*, 1950, **78**, 347.

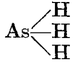
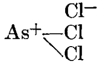
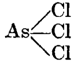
[41] L. O. Brockway, J. Y. Beach, and L. Pauling, *J. Amer. Chem. Soc.*, 1935, **57**, 2693 ; 1937, **59**, 2181.

[42] R. Bersohn, *J. Chem. Phys.*, 1954, **22**, 2078.

[43] C. A. Burrus and W. Gordy, *Phys. Rev.*, 1953, **92**, 274.

[44] W. Gordy, in " Chemical Applications of Spectroscopy ", Interscience Publishers, New York, Ch. 2.

Table 5. *Structure of molecules and values of unbalanced* p *valence electrons*

Nucleus	Ref.	Molecule	Contributing structures	Hybridisation	U_p for each structure	Importance (%)	Net U_p	U_p (obs.)
Cl . . .	3	FCl	F:Cl	None	1·00	75	1·37	1·33
			$F^{-}Cl^{+}$		2·30	25		
,, . . .	3	ICl	I:Cl	15% *s*	0·85	85	0·72	0·753
			$I^{+}Cl^{-}$		0	15		
,, . . .	1	ICl	I:Cl	None	1·00	75	0·75	0·753
			$I^{+}Cl^{-}$		0	25		
,, . . .	3	TlCl	Tl:Cl	15% *s*	0·85	18	0·15	0·144
			$Tl^{+}Cl^{-}$		0	82		
,, . . .	1	TlCl	Tl:Cl	None	1·00	20	0·14	0·144
			$Tl^{+}Cl^{-}$		0	80		
,, . . .	3	SiH_3Cl	$H_3Si—Cl$	15%	0·85	30		
			$H_3Si^{+}Cl^{-}$		0	40	0·38	0·36
			$H_3Si^{-}{=}Cl^{+}$	15% *σ* bond	0·40	30		
,, . . .	1	SiH_3Cl	$H_3Si—Cl$	None	1·00	40	0·40	0·36
			$H_3Si^{+}Cl^{-}$		0	60		
As . . .	1	AsH_3		9% *s*	— 0·30	100	— 0·30	— 0·28
,, . . .	3	$AsCl_3$		10%	— 0·25	50		
,, . . .					— 0·30	50	— 0·28	— 0·29

bonding of ionic character and hybridisation. The problem is simplified when crystal-structure data are available.

The large asymmetry parameter, $\varepsilon = 0{\cdot}15$, found in solid iodine by Dehmelt [45] reveals the presence of weak cross-bonding between the I_2 molecules in the crystalline sheets. Townes and Dailey [46] believe that the covalent bond from a given iodine atom resonates between its partner in the molecule and the two nearest neighbouring atoms belonging to other I_2 molecules in the crystal. These auxiliary cross-bonds are each calculated to have an importance of 9% ; the main molecular I_2 bond thus having an importance of 82%. An alternative explanation has been put forward by Robinson, Dehmelt, and Gordy [36] who point out that the *sp* hybrid bonds suggested by Townes and Dailey do not explain the formation of planar sheets of I_2 molecules in the crystal. Robinson, Dehmelt, and Gordy suggest that the cross-bonding arises as a result of the employment of the 5*d* orbitals to increase the valence of iodine. If it is assumed that the iodine atoms use hybrid *spd* orbitals for bonding the planar arrangement of the atoms in the crystal is more readily explained.

Where the crystal structure of a substance is unknown a complete analysis is impossible. Useful information has been obtained by studying a series of similar compounds.[47] In interpreting these results it is generally assumed that the solid-state effects can be neglected, since they are not large for slightly polar molecules, and do not vary much from one member of the series to the next.

Pure quadrupole spectra of aliphatic chlorine compounds have been obtained by Livingston.[48] He was led to the conclusion that the replacement of hydrogen by a more electronegative atom such as a halogen reduced the ionic character of the C–Cl bond. The ionic character of a C–Cl bond in an aliphatic chlorine compound was increased by the replacement of a hydrogen atom with a more electropositive group such as CH_3.

A great deal of information of value to organic chemists has already been obtained. Of particular interest is the variation in the Cl coupling in substituted chlorobenzenes with the nature and position of the substituent.[49] A close correlation was found with Hammett's substituent parameter σ.[50] A relation between the resonance frequency and σ is to be expected since both parameters depend on the electron density of the bonding electrons. Meal [51] has shown that the correlation is not as good when the substituent group is a complicated polar group ; presumably these groups lead to large interactions in the solid state. Bray and Barnes,[52] in a similar fashion, have compared the resonance frequencies

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[45] H. G. Dehmelt, *Naturwiss.*, 1950, **17**, 398.

[46] C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, 1952, **20**, 35.

[47] A. L. Schawlow, *ibid.*, 1954, **22**, 1211.

[48] R. Livingston, *ibid.*, 1951, **19**, 1434, 1613 ; 1952, **20**, 1170.

[49] E. Bright Wilson, *Ann. New York Acad. Sci.*, 1952, **55**, 943.

[50] L. P. Hammett, " Physical Organic Chemistry ", McGraw-Hill Book Co. Inc., New York, 1940, Ch. 7.

[51] H. C. Meal, *J. Amer. Chem. Soc.*, 1952, **74**, 6121.

[52] P. J. Bray and R. G. Barnes, *J. Chem. Phys.*, 1954, **22**, 2023.

of the ^{81}Br isotope in bromobenzene derivatives with the electron density in the vicinity of the carbon atom to which the bromine is bonded.

Studies have been carried out on the Group IV tetrahalides.[36, 47] The possibility of the links to the halogen atoms having some double-bond character complicates the analysis of these results. There are clear indications, however, that there is an increase in ionic character in going from carbon to tin with a corresponding decrease in double-bond character from silicon to tin. Duchesne and Monfils [53] have shown that the average values of the quadrupole coupling constant for the chlorine atoms in varying relative positions as one goes from C_6H_5Cl to C_6Cl_6 are linearly related to the number of chlorine atoms. They suggest that the increase in the coupling constant in going from *m*-dichlorobenzene to *o*-dichlorobenzene is due to the twisting of the C–Cl bonds in the non-planar *ortho*-compound. Bersohn,[42] however, suggests that an inductive effect is primarily responsible for the change in the coupling constant.

Other valuable solid-state studies are listed by Dehmelt.[54]

Applications.—The use of coupling constants in obtaining information on the electronic structure of molecules has been emphasised in this Review.

In certain cases coupling constants give direct information on the valence states of atoms in molecules. When nitrogen is triply bonded, as in ammonia and the X·CN series, the ^{14}N coupling constant is about – 4 Mc./sec. (Table 6). The molecules CH_3·NC and NNO possess quadrivalent nitrogen atoms whose coupling constants are found to be very small since the surrounding valence-shell electrons are nearly spherically distributed.

In this manner coupling constants afford a new and powerful source of information about the type of bonding associated with atoms in molecules.

TABLE 6. *Quadrupole coupling constants of* ^{14}N *and* ^{33}S

Molecule	*eQq* (Mc./sec.)	Molecule	*eQq* (Mc./sec.)	Molecule	*eQq* (Mc./sec.)
H·CN	– 4·58	NH_3	– 4·084	H·NCS	+ 1·20 (N)
CH_3·CN	– 4·40	ON′N″	– 0·08 (N′)	H·NCS	– 27·5 (S)
H·C≡C·CN	– 4·20	CH_3·NC	+ 0·5	OCS	– 29·1 (S)

As values for groups of substances containing structural linkages in common accumulate, it will be possible to relate certain ranges of coupling constant with specific structural units. The value of coupling constants in this respect is illustrated by the widely differing coupling constants obtained for ^{14}N for the —C≡N and —N≡C links (Table 6).

The great similarity in electronic structure of the C–S bonds in H·NCS and OCS is emphasised by the approximately equal values obtained for the ^{33}S coupling constants. The value obtained for the ^{14}N coupling constant proves conclusively [55] that the molecule is H·NCS and not H·SCN.

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[53] J. Duchesne and A. Monfils, *J. Chem. Phys.*, 1954, **22**, 562.

[54] H. G. Dehmelt, *Discuss. Faraday Soc.*, 1955, **19**, 263.

[55] G. C. Dousmanis, T. M. Sanders, and H. J. Zeiger, *J. Chem. Phys.*, 1953, **21**, 1416; C. H. Townes and S. Geschwind, *Phys. Rev.*, 1948, **74**, 626.

A number of substances have been studied in the gas phase and in the solid phase. No great variation in coupling constant is found (Table 7).

TABLE 7. *Nuclear quadrupole coupling constants in the solid and the gaseous state*

Molecule	Nucleus	*eQq* (Mc./sec.)	
		Solid	Gas
$CH_3{\cdot}I$	^{127}I	1753	1931·5
ICN	^{127}I	2549	2420
ICI	^{127}I	3037	2944
$CH_3{\cdot}Br$	^{79}Br	528·9	577·0
CH_2Cl_2	^{35}Cl	71·98	78
$CH_3{\cdot}Cl$	^{35}Cl	68·40	75·13
$CF_3{\cdot}Cl$	^{35}Cl	77·58	78·05

There is fair agreement between the values measured in the solid and in the gas phase. Such comparisons can be used to study the changes in valence bonding associated with a change in phase.

Valuable information on the crystal structure of substances can be obtained by single-crystal studies. For example, the number and symmetry of non-equivalent lattice sites in a crystal occupied by the same atomic species can be obtained since the field gradients at the nuclei are not identical.[56] For many substances only a single Cl resonance line is observed but in certain crystals a large number of closely spaced lines are observed.[48] In addition the Zeeman effect of nuclear quadrupole resonance lines can be used to determine the direction of covalent bonds with respect to the crystal lattice. This information is of great value in simplifying the *X*-ray analysis of crystal structures.

Additional solid-state information can be obtained by studying the shapes, widths, and the temperature-dependence of nuclear quadrupole resonance lines. Dehmelt and Krüger [57] attribute the temperature dependence of the Cl quadrupole spectra in *trans*-dichloroethylene to a variation in the amplitude of the torsional oscillations of the molecule, which thereby changes the average field gradient effective at the chlorine nucleus.

It is obvious that a great deal of new information about the solid state will be obtained from nuclear quadrupole resonance studies.

Conclusion.—It is clear that the measurements of nuclear quadrupole coupling constants are of great importance for the elucidation of problems concerned with the nature of valence bonds. This new type of experimental evidence will supplement data such as bond energies, dipole moments, and polarisabilities which have hitherto served to test electronic wave-functions. Moreover it is important to point out that coupling constants are sensitive to the electronic distribution near the nucleus and not to the electronic

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[56] H. G. Dehmelt, *Z. Physik,* 1951, **130,** 385.

[57] H. G. Dehmelt and H. Krüger, *ibid.,* 1951, **129,** 401.

distribution in the overlap region of the valence bond. In this region, near the nucleus, the adequacy or otherwise of wave-functions has not previously been tested. It is clear that a difficulty arises if wave-functions are normalised in the usual manner. For bonds possessing a mixed character the values obtained for the amounts of ionic character and *sp* hybridisation are not unique since it is impossible to obtain two unknown quantities from a single quadrupole coupling measurement.

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