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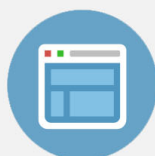
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## Determination of Electronic Structure of Molecules from Nuclear Quadrupole Effects

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Nuclear quadrupole coupling constants in molecules depend on the nuclear quadrupole moments and the variation in electrostatic field at the nucleus. It is shown that this variation of electric field is usually simply related to the molecular electronic structure, being primarily dependent on the way in which valence electrons fill the lowest-energy *p*-type orbits. Structural information which can consequently be obtained from known quadrupole coupling constants is discussed. Hybridization of the normal covalent bonds of N, Cl, and As with at least 15 percent *s* character is clearly shown. The alkali halides appear to be almost purely ionic; the quadrupole coupling data allow no more than 3 percent covalent character. In addition to molecular structure, some nuclear quadrupole moments are approximately evaluated by use of the theory developed here.

**M**OLECULAR constants called nuclear quadrupole coupling constants have already been measured by means of radio spectroscopy for about fifteen nuclei in twice as many molecules, and future measurements will probably provide many more cases. This coupling constant depends on the quadrupole moment of the nucleus and the second derivatives of the electrostatic potential at the nucleus due to all molecular charges outside the nucleus. The quadrupole moment  $Q$  is a characteristic of the particular nucleus and is a measure of the departure of the nuclear charge distribution from spherical shape. Thus an "elongated" nucleus has a positive  $Q$  and a "flattened" nucleus a negative  $Q$ . If the molecular electric field acting on the nuclear charges changes rapidly with angle from some molecular axis, then various orientations of a non-spherical nucleus with respect to this axis give various energies. The quadrupole coupling constant is a measure of this variation of electrostatic energy with orientation of the nucleus. In a linear or symmetric top molecule, the quadrupole coupling may be specified by one constant, which may be written  $eQ(\partial^2 V/\partial z^2)$ , where  $e$  is the protonic charge,  $Q$  the nuclear quadrupole moment,  $V$  the electrostatic potential, and  $z$  the coordinate along the molecular axis.<sup>1,2</sup> Complete description

of quadrupole effects in asymmetric molecules requires two constants instead of one, but in many cases a similar single constant is expected to be adequate.<sup>3</sup>

In order to calculate  $\partial^2 V/\partial z^2$  (hereinafter often abbreviated to  $q$ ), the distribution of charges in the molecule must be known, which entails primarily a determination of wave functions for the electrons. A straightforward theoretical determination of these quantities is usually very complex, and only for the hydrogen molecule<sup>4</sup> has a value of  $q$  been obtained by determination of an accurate wave function and subsequent calculation of  $\partial^2 V/\partial z^2$ . A method of approximating  $q$  has been previously suggested,<sup>5</sup> and will be developed more fully below.

Approximate wave functions are frequently used to explain, in at least a qualitative way, various molecular properties. Thus when the chemist writes down a structural formula for a molecule, he is making a guess at the distribution of charges in the molecule, or specifying an approximation to the molecular wave function. Such a structural formula, or the wave function in terms of which it may be expressed, allows approximate calculation of such quantities as dipole moment, internuclear distances, bond angles, and binding energy. Useful and, in some cases, fairly accurate information can also be obtained about  $q$  from structural considerations because  $q$  depends on a few rather simple parameters of bond structure.

The magnitude of  $q$  at a nucleus depends almost entirely on the way in which the lowest available *p*-type orbits are occupied by valence electrons surrounding the nucleus. An *s*-type orbit or any closed shell of electrons is spherically symmetric and hence gives no contribution to the variation of energy with nuclear ori-

TABLE I. Quadrupole coupling constants of Cl<sup>35</sup>.

Molecule	Most important structure	Quadrupole coupling constant $eQq$ in megacycles/sec.
Atomic Cl		-110.4
ICl	I—Cl	- 82.5
ClCN	Cl—C≡N	- 83.2
CH <sub>3</sub> Cl	H <sub>3</sub> C—Cl	- 75.13
NaCl	Na <sup>+</sup> Cl <sup>-</sup>	< 1

\* Work supported by the Signal Corps.

<sup>1</sup> J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey, and H. R. Zacharias, *Phys. Rev.* **57**, 677 (1940).

<sup>2</sup> J. H. Van Vleck, *Phys. Rev.* **71**, 468 (1947); D. K. Coles and

W. E. Good, *Phys. Rev.* **70**, 979 (1946); J. Bardeen and C. H. Townes, *Phys. Rev.* **73**, 97 (1948).

<sup>3</sup> J. K. Bragg, *Phys. Rev.* **74**, 533 (1948).

<sup>4</sup> A. Nordsieck, *Phys. Rev.* **58**, 310 (1940).

<sup>5</sup> C. H. Townes, *Phys. Rev.* **71**, 909 (1947).

entation or to  $\partial^2 V / \partial z^2$  at the nucleus.\*\* However, a  $p$ -type orbit gives the necessary variation of charge distribution with angle and because it gives the electron considerable probability of being near the nucleus, the effect of the lowest-energy  $p$ -type orbit is usually considerably greater than that of any other orbit or of any charges on nearby atoms in the molecule. In addition, distortion of the lowest-energy  $p$  orbit by hybridization or combination with other orbits can be shown to produce little effect on its contribution to  $q$  except by decreasing the importance of the  $p$  orbit as a result of normalization of the wave function.

Consider as an example the chlorine atom. As a neutral atom, it lacks one  $p$  electron from completing a closed spherical shell of charge, and hence shows a rather large value of  $q$ . If chlorine is covalently bonded in a molecule, the simplest idea of its bond would indicate that it lacks one  $p$  electron (oriented along the bond axis) from having a spherical shell, and that again  $q$  should be large and approximately equal to its value for a free atom. If the chlorine accumulates an extra electron and is ionic either as a free ion or in a molecule, there is no  $p$ -electron defect from a closed shell, and  $q$  might be expected to be very small or zero. That this description gives a good first approximation to  $q$  can be readily seen from a comparison in Table I of quadrupole coupling constants  $eqQ$  for the chlorine atom and for chlorine covalently or ionically bonded in various molecules. Table I applies to the nucleus  $\text{Cl}^{35}$  only; similar results are available for  $\text{Cl}^{37}$  which has a slightly smaller value of  $Q$  than does  $\text{Cl}^{35}$ .

Chlorine covalently bonded in various molecules shows a fairly constant quadrupole coupling and one which is not far from the value for atomic Cl. The strikingly low value of  $eqQ$  for NaCl indicates the very great difference between its bond and those of the other molecules listed, and that NaCl must involve only a very small amount of covalent character. That couplings for covalently bonded Cl are approximately 25 percent less than the value for atomic Cl will be shown below to be good evidence that the covalent Cl bond is an  $s-p$  hybrid. In addition, the small variations in  $eqQ$  between various covalent cases are useful information and will be discussed.

Another example is afforded by a comparison of coupling constants of  $\text{N}^{14}$  given in Table II. For all molecules where  $\text{N}^{14}$  is triply bonded ( $\text{NH}_3$ ,  $\text{HCN}$ ,  $\text{ClCN}$ , and  $\text{CH}_3\text{CN}$ ), the coupling constant is about 4 megacycles. For the two known cases where  $\text{N}^{14}$  is rather surely quadruply bonded ( $\text{CH}_3\text{NC}$  and the central nitrogen in  $\text{N}_2\text{O}$ ) so that a complete valence shell is filled and the surrounding electrons therefore nearly

spherically distributed, the coupling constant is less than 0.5 Mc.

Thus quadrupole coupling constants afford a new source of information about the character of molecular bonds, a source which in some cases appears to give different and more reliable information than is otherwise available. In addition, experimentally measured quadrupole coupling constants can be used to evaluate nuclear quadrupole moments in case the molecular or bond structure is sufficiently well known to allow determination of  $\partial^2 V / \partial z^2$  by the approach outlined here. Of

TABLE II. Quadrupole coupling constants of  $\text{N}^{14}$ .

Molecule	Most important structures	Quadrupole coupling constant $eqQ$ in megacycles/sec.
$\text{NH}_3$	$\begin{array}{c} \text{H} \\ \diagup \\ \text{N}-\text{H} \\ \diagdown \\ \text{H} \end{array}$	$\pm 4.10$
$\text{HCN}$	$\text{H}-\text{C}\equiv\text{N}$	-4.7
$\text{CH}_3\text{CN}$	$\text{H}_3\text{C}\equiv\text{N}$	-4.67
$\text{BrCN}$	$\text{Br}-\text{C}\equiv\text{N}$	-3.83
$\text{CH}_3\text{NC}$	$\text{H}_3\text{C}-\text{N}^+\equiv\text{C}^-$	<0.5
$\text{N}_2\text{O}$	$\text{N}\equiv\text{N}^+-\text{O}^-, \text{N}^+=\text{N}=\text{O}$	-0.27 (central N)

course, for a measurable coupling constant the nuclear quadrupole moment must not be zero. Since the nuclear quadrupole moment can be shown to be zero for all nuclei of spin less than one, some chemical elements show no quadrupole effects and give no information of the type considered here. But the  $\text{N}^{14}$  and  $\text{S}^{33}$  nuclei and all of the halogens excepting F show these effects, as well as a large number of nuclei less commonly encountered.

We will attempt below to justify and make more quantitative the procedure for evaluating  $q$  which has been suggested, and discuss most of the molecules for which quadrupole coupling constants have been measured with the purpose of testing this procedure and of obtaining information about the structure of the molecular bonds involved.

#### QUADRUPOLE COUPLING IN ATOMS

Before discussing in detail the evaluation of quadrupole coupling constants in molecules, we shall consider the simpler atomic case. In this case it can readily be shown that, neglecting spin effects, the value of  $\partial^2 V / \partial z^2$  at the nucleus due to a single electron of orbital angular momentum  $l$  is  $-(2le/2l+3)\langle r^{-3} \rangle$ , where  $e$  is the electronic charge and  $\langle r^{-3} \rangle$  is the average of the inverse third power of the distance between the nucleus and electron. In this case  $z$  represents some fixed direction in space and the atom is assumed to be in such a state that the projection of  $l$  on  $z$  has its maximum value ( $m=l$ ). For

\*\* One might object that an  $s$ -type orbit produces a charge density  $\rho$  at the nucleus which from Poisson's equation gives a value  $-4\pi\rho/3$  to  $\partial^2 V / \partial z^2$  at the nucleus. Because of spherical symmetry, however, this contribution produces no energy change with nuclear orientation and is specifically omitted from  $\partial^2 V / \partial z^2$  which was defined above as the second derivative of the potential produced by all molecular charges outside the nucleus.

a hydrogen-like electronic wave function,

$$\langle r^{-3} \rangle = Z^3/n^3 a_0^3 l(l+\frac{1}{2})(l+1), \quad (1)$$

where  $Z$  is the number of protonic charges on the nucleus,  $n$  the total quantum number, and  $a_0$  the Bohr radius 0.53A.

A closed shell of electrons around a nucleus produces a spherically symmetric charge distribution for which  $\partial^2 V/\partial z^2$  at the nucleus is zero. If, in addition to closed shells, there is one valence electron, then to take into account screening effects one must use an effective value of  $Z$  or of  $n$  in expression (1). There are fortunately other spectroscopically determinable quantities which involve  $\langle r^{-3} \rangle$ , namely, the atomic fine structure due to spin-orbit coupling, and hyperfine structure connected with a nuclear magnetic moment. In many cases  $\langle r^{-3} \rangle$ , or good values for the effective  $Z$  or  $n$ , may therefore be determined experimentally. Thus, using the fine structure doublet separation  $\Delta\nu$ , one obtains<sup>6</sup>

$$(\partial\nu/\partial z^2)_{\text{atom}} = -2le\Delta\nu/Z_i R\alpha^2 a_0^3 (l+\frac{1}{2})(2l+3), \quad (2)$$

where  $Z_i$  is the effective "unscreened" value of  $Z$  defined by Landé and for  $p$  electrons may usually be taken as the atomic number of the nucleus less four.  $R$  and  $\alpha$  are the Rydberg and fine structure constants, respectively. In case the nuclear gyromagnetic ratio and the resulting hyperfine structure are known, one may use the following expression<sup>6</sup> which completely eliminates the uncertainties of "effective"  $Z$  and  $n$ ,

$$(\partial^2 V/\partial z^2)_{\text{atom}} = -\frac{aeM}{g_I \mu_0 m} \frac{J(J+1)}{(l+1)(2l+3)}, \quad (3)$$

where  $e$ ,  $m$ =electronic charge and mass, respectively,  $\mu_0$ =Bohr magnetron,  $M$ =proton mass,  $J$ =total angular momentum of the electron ( $l$  plus spin),  $g_I$ =gyromagnetic ratio of nucleus of spin  $I$ , and  $a$ =hyperfine structure parameter such that energy of magnetic interaction of nucleus and electron is  $a(I \cdot J)$ .

The case of interactions between the nucleus and more than one electron is somewhat more complex and can be less exactly evaluated. A few of such cases, as well as corrections for relativistic effects, are discussed by Casimir.<sup>7</sup>

#### QUADRUPOLE COUPLING IN MOLECULES—GENERAL CONSIDERATIONS

To evaluate  $\partial^2 V/\partial z^2$  at a particular nucleus in a molecule, we shall discuss separately the contributions of valence electrons which have a high probability of being found near this nucleus, of the inner core of electrons which are definitely associated with the nucleus and whose contribution undergoes relative small

changes due to location of the atom in a molecule, and, finally, of the remaining charges in the molecule such as electrons and ions at distances of an atomic radius and more from the nucleus in question. The problem of computing exactly the contributions to  $q$  from these different sources is obviously a complex one and requires a rather complete knowledge of the molecular wave function. We shall examine here the character and relative size of the various contributions, and find that in many cases one or two simple terms give the dominating contributions to the quantity to be computed, and hence these cases lend themselves to a rather simple approximate evaluation of  $q$ .

Consider first an atom with one valence electron outside of a closed shell. The wave function for this electron in a molecule may be expanded in terms of the atomic wave functions  $\psi_{nlm}$ ; thus

$$\psi = \sum_{nlm} a_{nlm} \psi_{nlm}. \quad (4)$$

Of course, the electron wave functions may be expanded in somewhat different functions, such as the  $p_x$ ,  $p_y$ , and  $p_z$  orbitals often used in discussions of molecular bonds, but for convenience we have chosen atomic wave functions designated as usual by  $n$ ,  $l$ , and  $m$ —the total quantum number, azimuthal, and magnetic quantum numbers, respectively. The lowest energy atomic orbits not occupied by electrons forming closed shells may be expected to be present most importantly in the molecular wave function of the valence electron. Thus usually  $a_{nlm}$  will be largest for the lowest allowed values of  $n$  and  $l$ . Of course, expression (4) must provide some probability of the electron's being found in an approximately atomic orbit of an adjacent atom to which it forms a bond. This results in the presence of a number of atomic wave functions of rather large  $n$  and  $l$ , each, however, with rather small coefficients  $a_{nlm}$  by comparison with the lowest atomic energy states of the particular atom on which our attention is centered.

TABLE III. Relative values of electronic quadrupole field  $q_{nl0} \equiv (\partial^2 V/\partial z^2)_{n,l,m=0}$  for various atomic states. The very large effect of screening is shown by comparison of the third and fourth columns.

Electronic state	Atomic example for which fine structure is known	Values of $q_{nl0}$ from fine structure	Relative values of $q_{nl0}$ assuming hydrogen wave functions and no screening (Eq. (7))
			Relative to 5p
5p	I	$45 \times 10^{15}$ e.s.u.	1.00
5d	Cs	$0.31 \times 10^{15}$	0.14
5f	Cs		0.048
6p	Cs	$3.4 \times 10^{15}$	0.58
6d	Cs	$0.16 \times 10^{15}$	0.08
6f	Cs		0.028
7p	Cs	$1.1 \times 10^{15}$	0.36
7d	Cs	$0.09 \times 10^{15}$	0.05
			Relative to 2p
2p	F	$21 \times 10^{15}$	1.00
3p	Na	$0.7 \times 10^{15}$	0.30
4p	Na	$0.2 \times 10^{15}$	0.12

<sup>6</sup> Cf. H. A. Bethe and R. F. Bacher, Rev. Mod. Phys. 8, 209 226 (1936).

<sup>7</sup> H. B. G. Casimir, *On the Interaction between Atomic Nuclei and Electrons* (Teyler's Tweede Genootschap, E. F. Bohn, Haarlem, 1936).

We choose the axis of the molecular bond as a reference direction for the magnetic quantum numbers  $m$ , and evaluate the contribution of this valence electron to  $\partial^2 V / \partial z^2$  at the nucleus. Since  $\partial^2 / \partial z^2 (e/r) = (3 \cos^2 \theta - 1)e/r^3$ , where  $\theta$  is the azimuthal angle with respect to the bond axis,

$$\partial^2 V / \partial z^2 = e \int \psi^* [(3 \cos^2 \theta - 1)/r^3] \psi d\tau.$$

Using the series expansion of  $\psi$  given in (4),

$$\frac{\partial^2 V}{\partial z^2} = \sum_{nlm} |a_{nlm}|^2 q_{nlm, nlm} + \sum_{nlm, n'l'm'} a_{nlm} a_{n'l'm'}^* q_{nlm, n'l'm'}, \quad (5)$$

where

$$q_{nlm, n'l'm'} = \int \psi_{nlm} [(3 \cos^2 \theta - 1)/r^3] \psi_{n'l'm'}^* d\tau$$

and the second sum is over all non-identical  $nl$  and  $n'l'$ , since all terms for which  $n=n'$  and  $l=l'$  are collected in the first sum. For a non-zero value of  $q_{nlm, n'l'm'}$ ,  $m$  must equal  $m'$ , and either  $l=l' \neq 0$  or  $l=l' \pm 2$ . This conveniently eliminates a large number of terms from the second sum of (5). To obtain a rough approximation to the magnitude of other terms of this part of (5), one may use hydrogen-like wave functions for the  $\psi_{nlm}$ .

The quantities  $q_{nlm, nlm}$  of (5) are simply the values of  $\partial^2 V / \partial z^2$  or  $q$  for each of the atomic states, and are multiplied by  $|a_{nlm}|^2$ , the fractional importance of the respective atomic states in the molecular wave function. It is quite significant that  $q_{nlm, nlm}$  (which we hereby shorten to  $q_{nlm}$ ) is a rapidly decreasing function of  $n$  and  $l$  except that for an  $s$  state  $q_{n0m} = 0$ . Hence the dominating term in the first sum of (5) will usually be the state of lowest allowed  $n$  because not only will energy considerations make the amplitude  $a_{nlm}$  of this wave function large but, in addition, the  $q_{nlm}$  for this state is considerably larger than for the higher energy states. We shall demonstrate this in more detail for the cases where  $m=0$ .

The value of  $q$  for the atomic state with  $m$ , or the projection of  $l$  on the  $z$  axis, equal to zero differs from that for the case of  $m=l$  discussed above by the factor  $-(l+1)/(2l-1)$ , so that

$$(\partial^2 V / \partial z^2)_{l, m=0} = [2l(l+1)/(2l-1)(2l+3)] \langle r^{-3} \rangle. \quad (6)$$

For hydrogenic wave functions, from Eq. (1)

$$q_{n10} = 4Z^3/n^3 a_0^3 (2l-1)(2l+1)(2l+3). \quad (7)$$

If the effects of screening around a heavy nucleus are allowed for,  $q_{n10}$  decreases still more rapidly with  $n$  and  $l$  than indicated by expression (7). Table III shows the relative magnitudes for various states  $nl$  and compares the relative values computed for the hydrogenic case (Eq. (7)) with those obtained from the fine structure splitting (expression (2) modified by the

factor  $-(l+1)/(2l-1)$ ). Due to dependence on  $n$  and to screening effects, the element  $q_{n10}$  for the  $5p$  state of iodine is fourteen times larger than that for the  $6p$  state of caesium, and similarly the value for the  $6p$  state of Cs is considerably larger than that for any other state of Cs, the most marked differences occurring with the change of  $l$  which produces a correspondingly large change in screening. Although fine structure measurements are less complete in F and Na, Table III shows that even in these light nuclei where screening effects are less important,  $q$  decreases very rapidly with increasing  $n$  or  $l$ .

We now examine in more detail the magnitudes of terms in the second sum of Eq. (5), remembering that only two types of terms exist, those for which  $l=l' \neq 0$  and for which  $l=l' \pm 2$ . An estimate of their size may be obtained by using hydrogenic wave functions with rough corrections for screening as indicated by Table III. Calculation with this type of wave function shows that  $q_{nlm, n'l'm}$  is slightly less than  $(q_{nlm} q_{n'l'm})^{1/2}$  except for the cases  $l=l' \pm 2$  and  $n=n'$  ( $q_{nlm, n'l'm}$  is then identically zero), or when  $l$  or  $l'$  equals zero.

If a  $p$ -type wave function is the largest component of the molecular wave function, cross-product terms involving its amplitude  $a_{n1m}$  might be expected to be the largest. The only terms of this type involve mixing of this  $p$  state with other  $p$  and  $f$  states. Consider the cross-product terms of the  $p$  state with an  $f$  state. If the two states have the same  $n$ , then the term  $q_{n1m, n3m}$  is zero for the hydrogenic case. Allowing for screening effects,  $q_{n1m, n3m}$  may not be exactly zero, but in any case it would be  $\leq (q_{n1m} q_{n3m})^{1/2}$ , so that from Table III  $q_{n1m, n3m} \leq 0.05 q_{n1m}$ . In addition, because energy considerations indicate that the contribution, or coefficient  $a_{n3m}$ , of  $f$ -type atomic states in the molecular wave function (4) would probably be small, it seems clear that contributions to  $\partial^2 V / \partial z^2$  in (5) of this type of term can be neglected.

The terms in (5) for which  $l=l'$  and  $n \neq n'$  are not so easily ruled out. An estimate of  $q_{510, 610}$  for iodine from Table III would make it about  $\frac{1}{3}$  the value of  $q_{510}$ , while  $q_{610} \approx q_{510}/10$ . Thus, taking as an example a wave function of the two terms  $\psi = a_{510} \psi_{510} + a_{610} \psi_{610}$ , from (5),

$$\partial^2 V / \partial z^2 \approx [|a_{510}|^2 + |a_{610}|^2 / 10 + \text{Real Part of } (2a_{510} a_{610}^* / 3)] q_{510}.$$

If  $a_{610}$  is not considerably smaller than  $a_{510}$ , the third term in brackets may be comparable in magnitude with the first. We must rely on present understanding of the chemical bond which shows that  $a_{610}$  probably is much smaller than  $a_{510}$ . Because an electron makes a bond only to one adjacent atom, the largest and most easily understood distortion of an atomic orbital due to molecular forces results in decreasing electron density on one side of the atom and increasing it on the other side. This may be accomplished by the well recognized addition of an  $s$  or  $d$  wave function to a  $p$  function. Thus a molecular wave function  $\psi = (\sqrt{3}/2) \psi_p + \frac{1}{2} \psi_s$  has been

shown by Pauling<sup>8</sup> to give a "stronger" molecular bond than a pure  $p$  function or any other combination of  $s$  and  $p$ . There are no similar good reasons for the electronic orbit to be much elongated or contracted in both directions along the bond-axis, which would be the result of adding appreciable atomic wave functions of the same angular symmetry. We shall thus dispose of terms in the second sum of (5) having  $l=l'$  by estimating that when the lowest available atomic orbital is a  $p$  state the amplitude of higher  $p$  states is less than 0.1, or, in the specific example given above,  $|a_{610}| < 0.1 |a_{510}|$ .

The only other type of cross-product term which needs consideration involves the  $s$  and  $d$  states. Here  $l=l'-2$ , so that the terms are not identically zero, and since an  $s$  type wave function is large near the nucleus, the value of  $q_{n00, n'20}$  may be expected to be large. Calculation of its magnitude with hydrogenic wave functions shows that  $q_{n00, n'20}$  is approximately equal to or slightly less than  $q_{n'10}$  when  $n \neq n'$ . Again if  $n=n'$ , this term is zero for the hydrogen-like case, but not necessarily zero when screening is taken into account. It is possible that in some of the heavier atoms where  $d$  orbits are expected to be important, terms due to mixing of  $s$  and  $d$  states will contribute appreciably to  $\partial^2 V / \partial z^2$ . However, for such a term,  $a_{n00} a_{n'20} q_{n00, n'20}$ , to be of importance compared with the contribution of the lowest  $p$  orbit, neither  $a_{n00}$  or  $a_{n'20}$  can be small. The molecular wave function must contain sizable components of both  $s$  and  $d$  atomic states.

Of course, there are other contributors to the value of  $q$  besides the valence electrons. Additional effects as mentioned above are due to the presence of other nuclei and shells of electrons associated with these nuclei in the remainder of the molecule, and to the possible polarization and distortion of what we have been calling the closed spherical shell of electrons around the nucleus under consideration.

An approximate magnitude for the effects of other charges in the molecule may be obtained by computing the contribution of one electronic charge placed a distance from the nucleus equal to the minimum internuclear distance. Thus one electronic charge placed one angstrom away contributes  $10^{+15}$  e.s.u. to the value of  $q$ . Table III shows that even for the light atom fluorine this is considerably less than the contribution of a valence electron in a low energy  $p$  state, and by comparison may be neglected. The value of  $q$  accurately calculated by Nordsieck<sup>4</sup> for the hydrogen molecule makes an interesting comparison. The two hydrogen atoms in the hydrogen molecule are closer (0.74Å) than any two atoms in any other molecule. Hence, one might expect the value of  $q$  resulting from distortion of the  $s$ -type electronic orbits and from the nearness of another nucleus to be the largest that would normally occur. Its value is  $1.15 \times 10^{+15}$  e.s.u.—approximately equivalent to one electron at a distance of one angstrom, and con-

siderably less than the  $q$  produced by a penetrating  $p$  electron.

We now turn to an examination of the effects of possible distortion of the core of electrons around the nucleus at which  $\partial^2 V / \partial z^2$  is to be determined. Consider a closed shell of three  $p$  orbits. A dipole may be induced on this shell because of adjacent charges which result, for example, in adding to the  $p$  electron with  $m=0$  along the axis some of the  $s$ -type wave function of the lowest available  $s$  state. Such a perturbation might give the  $s$ -type wave function an amplitude of about 0.1. Although this is enough polarization to effectively move 0.2 electron from one side of the core to the other, it does not greatly change the value of  $q$  at the nucleus. Contribution to  $q$  by this orbit will be decreased by only 1 percent, which is the decrease in the square of the amplitude of its normal  $p$  wave function. For the unperturbed spherical core, the two other  $p$  type orbits each contribute an amount half as large and opposite in sign to  $q$ , making it zero. If these orbits are perturbed, an amount similar to the perturbation of the  $m=0$  orbit, then their contributions decrease by the same fraction and  $q$  remains exactly zero. It may thus be seen that a rather large amount of polarization of this closed shell of electrons probably normally occurs without an appreciable effect on  $q$ . Of course, forces are present which may induce a quadrupole moment on the closed shell. Thus an  $f$ -type term might be added to the unperturbed  $p$  state. From the discussion of  $q_{nlm, n'l'm}$  above, it may be shown again that such a term produces only a small effect on  $q$ , and since the effect will be in the opposite direction from the quadrupole field due to charges adjacent to the atom under consideration, it will probably conveniently result in some reduction of their contribution to  $q$ .

Estimates show, then, that distortions of the closed shell of electrons surrounding the nucleus will produce contributions to  $q$  less than 1 percent of the value due to a single electron of the shell. Since such an electron is nearer the nucleus than the valence electron, this may be as large as 10 percent of the effect of the lowest  $p$  state of the valence electron.

Perhaps a more satisfying demonstration of the smallness of uncertainties due to polarization of the closed electron shell is given by examination of a few cases which allow effectively an experimental determination of their magnitude. The alkali halides are largely ionic molecules, so that they may be regarded as made up of two closed shells which are somewhat distorted by their mutual interaction. The amount of distortion may be judged from the dipole moment<sup>9</sup> of cesium fluoride, the alkali halide for which this moment is most accurately known. Its dipole moment is about 60 percent of the moment corresponding to unit positive and negative electronic charges separated by the distance between nuclei in this molecule. This reduction in dipole

<sup>8</sup> L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1945).

<sup>9</sup> H. K. Hughes, *Phys. Rev.* **70**, 570 (1946).

moment must be due to polarization of the ionic shells and possibly some admixture of the covalent state in the molecular wave function. This covalency will be shown below to be very small, but in any case if all three orbits of the outer shell of both Cs and F participate approximately equally in polarization effects, then the reduction in moment corresponds to perturbation or admixture of other states with amplitudes less than about 7 percent. This corresponds to the 10 percent somewhat arbitrarily chosen for the illustrative case above, and would on the same basis give a quadrupole coupling less than one two-hundredth that due to a single electron in one of these  $p$  orbits. Although the quadrupole moment of Cs is not known,<sup>10</sup> it would not be expected to be less than  $0.1 \times 10^{-24}$  cm<sup>2</sup>. Since the quadrupole coupling in CsF has been measured<sup>11</sup> as 1.24 megacycles,  $q$  at the Cs nucleus must be less than  $0.18 \times 10^{15}$  e.s.u., or less than one two-hundredth the contribution to be expected from a single  $p$  electron in the closed electron shell. Other alkali halides consistently show small quadrupole coupling constants for both the alkali and the halogen nuclei, indicating the smallness of the effects of distortion of the ionic shells on the value of  $q$  at the nuclei. Thus NaBr shows a rather small quadrupole coupling of 1.2 Mc due to Na and a coupling constant less than 1 Mc due to Br,<sup>12</sup> although atomic spectra and other molecules containing Br show quadrupole coupling constants of about 700 Mc.

As a result of the above considerations of the magnitudes of the various parts of (5), it can be said that to a fractional accuracy of the order of ten percent,  $\partial^2 V / \partial z^2$  due to a single valence electron can be regarded as simply a sum of contributions  $|a_{nlm}|^2 q_{nlm}$  from the various atomic states and, in addition, that if the lowest energy atomic state is a  $p$  state, contributions from other states may be neglected unless for some reason the amplitude of this  $p$  wave function in the complete molecular wave function is exceptionally small.

#### Detailed Example—ICl

The molecule ICl is perhaps the simplest case of a covalently bonded molecule for which nuclear quadrupole coupling constants are known. Since the approximations discussed above for obtaining  $q$  should be rather good in this case and an accurate value of the quadrupole moment of Cl is known from atomic data, we shall examine this case in detail as an introduction to the application of our method to other molecules.

For atomic Cl<sup>15</sup> in the ground state, the measurements of Davis *et al.*<sup>13</sup> give a value  $+55.2$  Mc\*\*\* for the nu-

clear quadrupole coupling constant  $(\partial^2 V / \partial z^2)_{\text{atom}}$  and allow an accurate evaluation of  $(\partial^2 V / \partial z^2)_{\text{atom}}$  from Eq. (3) as  $9.6 \times 10^{15}$  e.s.u. By comparison, the approximation methods of evaluating this quantity indicated by Eqs. (1) and (2) give  $6.0 \times 10^{15}$  and  $9.9 \times 10^{15}$  e.s.u., respectively. Of course, the ground state of chlorine involves one  $p$  electron missing from a closed shell, but essentially the same considerations apply to this case as to a single  $p$  electron outside closed shells.

The simplest reasonable assumption about the wave function of each of the two bonding electrons in ICl

TABLE IV. Bond distances used and some computed bond characters.

Molecule	Resonating structures	Percentage importance from bond # 1	Percentage importance from bond # 2	Observed bond distances (in angstroms)	Reference
ClCN	Cl—C≡N	75	90	Cl—C 1.620	a
	$\overset{+}{\text{Cl}}=\text{C}=\overset{-}{\text{N}}$	25	10	C—N 1.163	
BrCN	Br—C≡N	75	90	Br—C 1.790	a
	$\overset{+}{\text{Br}}=\text{C}=\overset{-}{\text{N}}$	25	10	C—N 1.158	
ICN	I—C≡N	76	90	I—C 1.995	a
	$\overset{+}{\text{I}}=\text{C}=\overset{-}{\text{N}}$	24	10	C—N 1.158	
NNO	$\overset{-}{\text{N}}=\overset{+}{\text{N}}=\text{O}$	50	100	N—N 1.126	b
	$\text{N} \equiv \overset{+}{\text{N}}-\overset{-}{\text{O}}$	50	0	N—O 1.191	
ICl				I—Cl 2.321	c
CH <sub>3</sub> Cl				C—H 1.107	d
				C—Cl 1.779	
CH <sub>3</sub> Br				C—H 1.100	d
				C—Br 1.940	
CH <sub>3</sub> I				C—H 1.100	d
				C—I 2.136	
AsF <sub>3</sub>				As—F 1.712	e
CH <sub>3</sub> CN				C—C 1.49	f
				C—N 1.16	
CH <sub>3</sub> NC				C—N 1.44	g
				N—C 1.18	
NH <sub>3</sub>				N—H 1.014	h
HCN				C—H 1.058	h
				C—N 1.157	

<sup>a</sup> C. H. Townes, A. N. Holden, and F. R. Merritt, *Phys. Rev.* **74**, 1113 (1948); A. G. Smith, H. Ring, W. V. Smith, and W. Gordy, *Phys. Rev.* **74**, 370 (1948).

<sup>b</sup> D. K. Coles, E. S. Elyash, and J. G. Gorman, *Phys. Rev.* **72**, 973 (1947).  
<sup>c</sup> G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939).

<sup>d</sup> W. Gordy, J. W. Simmons, and A. G. Smith, *Phys. Rev.* **74**, 243 (1948).  
<sup>e</sup> B. P. Dailey, K. Rusinow, R. Shulman, and C. H. Townes, *Phys. Rev.* to be published.

<sup>f</sup> L. Pauling, H. D. Springall, and K. J. Palmer, *J. Am. Chem. Soc.* **61**, 927 (1939).

<sup>g</sup> W. Gordy and L. Pauling, *J. Am. Chem. Soc.* **64**, 2952 (1942).

<sup>h</sup> G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945).

in the atomic state  $\partial^2 V / \partial z^2$  is usually evaluated for the state  $m=l$ , whereas in the molecular case the value for  $m=0$  is more convenient. In Table I the atomic value for the state  $m=0$  is needed to compare properly with molecular values of  $q$ .

<sup>10</sup> T. Schmidt, *Naturwiss.* **28**, 565 (1940).

<sup>11</sup> J. W. Trischka, *Phys. Rev.* **74**, 718 (1948).

<sup>12</sup> W. A. Nierenberg and N. F. Ramsey, *Phys. Rev.* **72**, 1075 (1947).

<sup>13</sup> L. Davis, Jr., B. T. Feld, C. W. Zabel, and J. R. Zacharias, *Phys. Rev.* **73**, 525 (1948).

\*\*\* Note that the value  $+55.2$  given here differs from the value  $-110.4$  of Table I by the factor  $-(l+1/2l-1)$  or  $-2$  because

TABLE V. Probable molecular structures and comparison of resulting quadrupole coupling constants with the observed values.

Nucleus	Molecule	Resonating structures	Percent-age im-portance	No. of "un-bal." $p$ electrons	No. for hybrid struc.	Assumed $eqQ$ per $p$ elec.	Coupling constant calculated	Coupling constant observed	Reference
$\text{Cl}^{35}$	$\text{ICl}$	$[\text{I}-\text{Cl}]$	91	0.82	0.75	- 110.4 Mc	- 83 Mc	- 82.5 Mc	a
		$^+\text{I}-\text{Cl}^-$	9	0					
$\text{Cl}^{35}$	$\text{CH}_3\text{Cl}$	$\text{CH}_3-\text{Cl}$	80	0.82	0.66	- 110.4	- 73	- 75.13	b
		$^+\text{CH}_3-\text{Cl}^-$	20	0					
$\text{Cl}^{35}$	$\text{ClCN}$	$\text{Cl}-\text{C}\equiv\text{N}$	83	0.82	0.75	- 110.4	- 83	- 83.2	c,d
		$^+\text{Cl}=\text{C}=\text{N}^-$	17	0.40					
$\text{Cl}^{35}$	$\text{NaCl}$	$^+\text{Na}-\text{Cl}^-$	97	0	<0.03	- 110.4	< 3	< 1	e
		$\text{Na}-\text{Cl}$	<3	1					
$\text{Br}^{79}$	$\text{CH}_3\text{Br}$	$\text{CH}_3-\text{Br}$	82	1	0.82	+ 720	+ 590	+ 577	b
		$^+\text{CH}_3-\text{Br}^-$	18	0					
$\text{Br}^{79}$	$\text{BrCN}$	$\text{Br}-\text{C}\equiv\text{N}$	85	1	0.96	+ 720	+ 680	+ 686.5	c, d
		$^+\text{Br}=\text{C}=\text{N}^-$	15	0.625					
$\text{Br}^{79}$	$\text{NaBr}$	$^+\text{Na}-\text{Br}^-$	97	0	<0.03	+ 720	< 21	< 1	e
		$\text{Na}-\text{Br}$	<3	1					
$\text{I}^{127}$	$\text{ICl}$	$[\text{I}-\text{Cl}]$	91	1	1.135	-2500	-2840	-2944	a
		$^+\text{I}-\text{Cl}^-$	9	2.5					
$\text{I}^{127}$	$\text{ICN}$	$\text{I}-\text{C}\equiv\text{N}$	87	1	0.951	-2500	-2380	-2420	c, d
		$^+\text{I}=\text{C}=\text{N}^-$	13	0.625					
$\text{I}^{127}$	$\text{CH}_3\text{I}$	$\text{CH}_3-\text{I}$	84	1	0.84	-2500	-2100	-1931.5	b
		$^+\text{CH}_3-\text{I}^-$	16	0					
$\text{As}^{75}$	$\text{AsF}_3$	$^+\text{As}-\text{F}^-$ F	100	-0.4	-0.4	600	- 240	- 235	f

<sup>a</sup> C. H. Townes, F. R. Merritt, and B. D. Wright, Phys. Rev. **73**, 1338 (1948).

<sup>b</sup> W. Gordy, J. W. Simmons, and A. G. Smith, Phys. Rev. **74**, 243 (1948).

<sup>c</sup> C. H. Townes, A. N. Holden, and F. R. Merritt, Phys. Rev. **74**, 1113 (1948).

<sup>d</sup> A. G. Smith, H. Ring, W. V. Smith, and W. Gordy, Phys. Rev. **74**, 370 (1948).

<sup>e</sup> W. A. Nierenberg and N. F. Ramsey, Phys. Rev. **72**, 1075 (1947).

<sup>f</sup> B. P. Dailey, K. Rusinow, R. Shulman, and C. H. Townes, Phys. Rev. to be published.

is that it represents a pure covalent bond made up only of the atomic ground states of I and Cl. Using a Heitler-London (atomic orbital) type of wave function for the two electrons involved in the covalent band, and indicating coordinates of the first electron by (1) and those of the second electron by (2),

$$\psi = a\{[\psi_{310}^{(1)}]_{\text{Cl}}[\psi_{510}^{(2)}]_{\text{I}} + [\psi_{310}^{(2)}]_{\text{Cl}}[\psi_{510}^{(1)}]_{\text{I}}\}. \quad (8)$$

The constant  $a$  is approximately  $1/\sqrt{2}$ , but must be modified a small amount because of the overlap of the iodine and chlorine wave functions, and will be  $1/(2+2S^2)^{1/2}$ , where  $S = \int [\psi_{310}]_{\text{Cl}}^* [\psi_{510}]_{\text{I}} d\tau$  is assumed for convenience to be real.

The value of  $q$  contributed by the first electron is

$$q_1 = e \int \psi^* [[3 \cos^2 \theta - 1]/r^3] \psi d\tau, \quad (9)$$

where  $\theta$  and  $r$  are coordinates of this electron. Inserting expression (8) for  $\psi$  and integrating,  $q_1 = [(q_{310} + Sq_s)/2(1+S^2)]$ , where  $q_s = \int [\psi_{310}^*]_{\text{Cl}} (3 \cos^2 \theta - 1)/r^3 [\psi_{510}]_{\text{I}} d\tau$ . The contribution due to the second electron is similar, so that both valence electrons in the state (8) give

$$q = [(q_{310} + Sq_s)/(1+S^2)] \approx q_{310}(1-S^2) + Sq_s. \quad (10)$$

To evaluate  $q_s$ , one might first try expanding  $[\psi_{510}]_{\text{I}}$  in terms of atomic wave functions about the Cl nucleus. This procedure is not very helpful because  $[\psi_{510}]_{\text{I}}$  will involve not only the Cl  $3p$  wave function, but also the  $2p$  and  $4p$  functions, which will give appreciable contributions to  $q_s$ . A more illuminating approach is to consider the character of the  $\psi_{310}$  wave function and the relative importance of its parts in contributing to  $(1/r^3)$ . For hydrogen,  $\psi_{310}$  has the form  $(2-r/3a_0)$



$\propto re^{-r/3a_0} \cos\theta$ , so that when  $\pi/2 < \theta < -\pi/2$ , there is a maximum at approximately  $r = 1.8a_0$ , a minimum at  $r = 10a_0$ , and a null at  $r = 6a_0$ . Integration shows that, although there is 90 percent probability of finding the electron at a distance  $r > 6a_0$ , or in the outer lobe of the probability distribution given by  $\psi_{310}$ , only 4 percent of the contribution to  $\langle 1/r^3 \rangle$  comes from the region  $r > 6a_0$ . Furthermore, only 14 percent of the contribution to  $\langle 1/r^3 \rangle$  comes from regions farther away than the first maximum, i.e.  $r > 1.8a_0$ . Again, simplification can be achieved because of the rapid variation of the function  $1/r^3$ , and only those parts of the integral for  $q_s$  need be considered which are closer to the nucleus than  $1.8a_0$ , or than the first maximum in the  $\psi_{310}$  probability distribution. If  $[\psi_{510}]_I$  were constant over this small region near the Cl nucleus,  $q_s$  would be essentially zero because of the reversal of the sign of  $\psi_{310}$  due to its dependence on  $\cos\theta$ . Actually  $[\psi_{510}]_I$  is not constant, but is small and slowly varying near the Cl nucleus. Using hydrogenic wave functions and appropriate screening constants,  $q_s$  can be roughly estimated as  $q_s = -0.05q_{310}$ . The sign of  $q_s$  is uniquely determined because of the relative phases of  $[\psi_{510}]_I$  and  $[\psi_{310}]_{Cl}$  must give a positive value to  $S$ . For the conclusions which follow, an exact evaluation of  $q_s$  is not as important as its sign, which depends primarily on the presence of one radial node in the  $\psi_{310}$  wave function, and not otherwise on its exact form.

Consider now the appropriateness of the wave function (8) or (9). It represents the lowest energy atomic state and a wave function which will at the same time contribute strongly to the exchange energy which is largely responsible for the chemical bond. The other lowest energy atomic states ( $m = \pm 1$ ) would contribute so little to chemical bonding that it is generally supposed they would be occupied by non-bonding electrons only. Some contributions to  $\psi$  may be made by higher energy atomic states, and in addition some of the lower energy atomic states such as the 3s state of Cl might be added to  $\psi$  by displacing the non-bonding electrons which would otherwise occupy these orbits. Since addition of an s or d wave function would increase the bond strength more than would a p function, the most likely additions to  $\psi$  would be 3s, 4s, and 3d wave functions. To allow for this hybridization,  $[\psi_{310}]_{Cl}$  in (8) may be replaced by

$$(1-b)^{1/2}[\psi_{310}]_{Cl} + \sum_{nlm} a_{nlm}[\psi_{nlm}]_{Cl},$$

where the sum is again over all chlorine atomic states except  $\psi_{310}$ , and the constant  $b$  is inserted to allow for the necessary renormalization of  $\psi$ . If no states lower than the 3s state are included in this hybridization, then to a good approximation the only effect of hybridization is through the renormalization constant  $b$ , and it may be shown that (10) is simply replaced by  $q = (1 + 2S^2 - b)q_{310}$ .

Possible ionic character of the ICl bond has not yet

been considered and terms in the wave function corresponding to a negatively charged chlorine and positively charged iodine ion must be included because chlorine is somewhat more electronegative than iodine. Ionic character of a bond or wave function has been used with several meanings and is not always precisely defined. As the quantity of importance in producing molecular dipoles, and whose magnitude is closely connected with electronegativity differences, it generally means the difference between the probabilities of finding a bonding electron on the two atoms with which it is associated. The same quantity is of importance in quadrupole coupling constants and is what is here referred to as "ionic character." This ionic character for a bonding wave function  $\psi$  constructed of atomic states  $\psi_1$  and  $\psi_2$  of each of two atoms as in (8) can be satisfactorily defined mathematically as

$$i = \frac{\int \left[ \int \psi_1^* \psi d\tau_1 \int \psi_1 \psi^* d\tau_1 - \int \psi_2^* \psi d\tau_1 \int \psi_2 \psi^* d\tau_1 \right] d\tau_2}{\int \int \psi^* \psi d\tau_1 d\tau_2}$$

where  $d\tau_1$  and  $d\tau_2$  represent volume elements for electrons 1 and 2, respectively, and  $\psi_1, \psi_2$  represent atomic states of atoms 1 and 2, respectively. If wave functions  $\psi_1$  and  $\psi_2$  for the two atoms enter symmetrically in the molecular wave function, this definition gives zero as the ionic character of the bond. Ionic character is allowed for in the wave function (8) by adding a term  $c[\psi_{310}^{(1)}]_{Cl}[\psi_{310}^{(2)}]_{Cl}$  corresponding to both electrons on the chlorine atom. After renormalization, this gives

$$\psi = \frac{1}{(1+S^2+c^2+2\sqrt{2}cS)^{1/2}} \times \left\{ \frac{[\psi_{310}^{(1)}]_{Cl}[\psi_{510}^{(2)}]_I + [\psi_{310}^{(2)}]_{Cl}[\psi_{510}^{(1)}]_I}{\sqrt{2}} + c[\psi_{310}^{(1)}]_{Cl}[\psi_{310}^{(2)}]_{Cl} \right\}$$

and  $i$  as defined above is  $c^2 + \sqrt{2}cS$  omitting cubic terms in  $c$  and  $S$ . The constant  $c$  is presumably positive to increase the exchange integral and produce a stronger chemical bond.

If the value of  $q$  contributed by two bonding electrons is computed for a molecular wave function including both hybridization and ionic character, it can, after some manipulation, be shown to be  $q = (1 - S^2 + c^2) \times q_{310} + 2(S + \sqrt{2}c)q_s$  neglecting powers of  $S$  and  $c$  higher than the second.

Although the inner closed shells of chlorine are expected to contribute a negligible amount to  $q$ , the other non-bonding electrons in the valence shell must be considered. It is customary to assume that the four non-bonding p electrons of Cl remain essentially in their atomic orbits if the chlorine is bonded normally in a molecule. We shall for the moment make this assumption so that their combined contribution to  $q$  is

$2q_{31-1} + 2q_{31+1}$ . Similarly, the two non-bonding  $s$  electrons of the valence shell remain in their atomic  $s$  orbitals unless some of this orbit has been used by the bonding electrons, in which case they would occupy the lowest available energy level, corresponding to a hybrid  $s$  and  $p$  orbit,

$$\psi = (d)\frac{1}{2}\psi_{300} + (j)\frac{1}{2}\psi_{310}.$$

Their contribution to  $q$  is then  $2fq_{310}$ . Now since for a completely filled shell,  $q=0$ , it can easily be seen that  $q_{31-1} = q_{31+1} = -\frac{1}{2}q_{310}$ . Therefore,  $q = (-1 - S^2b + c^2)q_{310} + 2(S + \sqrt{2}c)q_s$ . Since  $f$  is non-zero primarily because part of the  $3s$  wave function has been used in producing a hybridized bond,  $b \geq f$ , and  $b$  may be written  $b = b' - f$ , so that

$$eQq = (-1 - S^2 + c^2 - b' + f)eQq_{310} + 2(S + \sqrt{2}c)eQq_s \quad (11)$$

where all the quantities in the bracket are positive and real except  $c$ , for which the sign is unknown. Now  $eQq_{310}$  is just the quadrupole coupling constant in the atomic case for  $m=0$  and equals  $-(l+1)/(2l-1)$  or  $-2$  times the coupling constant 55.2 Mc found for

atomic  $\text{Cl}^{35}$  by Davis *et al.*<sup>13</sup> The measured value of the  $\text{Cl}^{35}$  quadrupole coupling in  $\text{ICl}$  is  $-82.5$  Mc, so that

$$1 + S^2 - c^2 + b' - f - 2(S + \sqrt{2}c)q_s/q_{310} = 0.723 \quad (12)$$

The ionic character may be obtained approximately from the curve of ionic character *versus* difference in electronegativity, which gives  $i=0.08$ , or from the dipole moment of  $\text{ICl}$  which gives  $i=0.06$  if depolarizing and other disturbing effects are neglected. Substituting  $i=0.08$ , Eq. (12) becomes

$$1 + b' + S^2 + \sqrt{2}cS - 2(S + \sqrt{2}c)q_s/q_{310} - f = 0.80. \quad (13)$$

Equation (13) shows that hybridization of the bonding orbit with atomic orbitals of higher energy would tend to increase the  $\text{ICl}$  quadrupole coupling constant, since this represents an increase in  $b'$ , whereas  $3s-3p$  hybridization of the bond gives a decrease in this constant. Since  $S$ ,  $b'$ , and  $c$  are positive and  $q_s/q_{310}$  negative,  $f \geq 0.20$ , corresponding to considerable  $3s-3p$  hybridization.

A similar type of calculation may be made using as a basis the Hund-Mulliken molecular orbital type of

TABLE VIa. Coupling constants for molecules containing nitrogen.  $\frac{1}{2}\psi_s + (\frac{3}{2})\frac{1}{2}\psi_p$  hybridization is assumed for  $\sigma$ -component of multiple bonds (see text).

Molecule	Resonating structures	% Importance	No. of "un-bal." $p$ electrons	No. for hybrid struc.	Assumed $eQq$ per $p$ elec.	Coupling constant calculated	Coupling constant observed	Reference
$\text{NH}_3$	$\text{N} \equiv \text{H}_3$	100	-0.16	-0.16	+24 Mc	-3.9	$\pm 4.10$ Mc	a
	$\begin{pmatrix} \text{H} \\   \\ \text{N}-\text{H} \\   \\ \text{H} \end{pmatrix}$	(100)	(-0.40)	(-0.40)	(+24)	(-9.6)	( $\pm 4.10$ )	
$\text{CH}_3\text{CN}$	$\text{CH}_3-\text{C} \equiv \text{N}$	85	-0.25	-0.18	+24	-4.4	-4.67	b
	$\text{CH}_3-\text{C}^+=\text{N}^-$	5	+0.20					
	$\text{H}^+\text{CH}_2-\text{C}=\text{N}^-$	10	+0.20					
$\text{HCN}$	$\text{H}-\text{C} \equiv \text{N}$	90	-0.25	-0.20	+24	-4.8	-4.7	c
	$\text{H}-\text{C}^+=\text{N}^-$	10	+0.20					
$\text{CH}_3\text{NC}$	$\text{CH}_3-\text{N}=\text{C}$	5	+0.25	+0.025	+24	+0.62	<0.5	b
	$\text{CH}_3-\text{N}^+ \equiv \text{C}^-$	95	0					
$\text{BrCN}$	$\text{Br}-\text{C} \equiv \text{N}$	80	-0.25	-0.166	+24	-3.8	-3.83	d
	$\text{Br}^+-\text{C}=\text{N}^-$	20	+0.20	-0.16				
$\text{NNO}$ (end nitrogen)	$\text{N}=\text{N}^+=\text{O}$	45	+0.20	-0.05	+24	-1.2	-1.03	e
	$\text{N} \equiv \text{N}-\text{O}^-$	55	-0.25					
$\text{NNO}$ (central nitrogen)	$\text{N}=\text{N}^+=\text{O}$	45	0.0	0.0	+24	0.0	-0.27	f
	$\text{N} \equiv \text{N}-\text{O}^-$	55	0.0					

\* R. S. Henderson, *Phys. Rev.* **74**, 107 (1948); The sign of  $eQq$  in  $\text{NH}_3$  has not definitely been established experimentally. However, if it is assumed that the magnetic field produced by molecular rotation is in the same direction as in other known cases, then the combination of nuclear quadrupole and dipole effects show that  $eQq$  is negative as is expected here.

<sup>b</sup> H. Ring, H. Edwards, M. Kessler, and W. Gordy, *Phys. Rev.* **72**, 1262 (1947).

<sup>c</sup> W. Gordy, *Phys. Rev.* to be published.

<sup>d</sup> C. H. Townes, A. N. Holden, and F. R. Merritt, *Phys. Rev.* **74**, 1113 (1948).

<sup>e</sup> A. G. Smith, H. Ring, W. V. Smith, and W. Gordy, *Phys. Rev.* **73**, 633 (1948).

<sup>f</sup> D. K. Coles, E. S. Elyash, and J. G. Gorman, *Phys. Rev.* **72**, 973 (1947).

TABLE VIb. Coupling constants for molecules containing nitrogen.  $(\frac{1}{2})^1\psi_s + (\frac{1}{2})^1\psi_p$  hybridization is assumed for  $\sigma$ -component of multiple bonds (see text).

Molecule	Resonating structures	% Importance	No. of "unbal." $p$ electrons	No. for hybrid struc.	Assumed $eqQ$ per $p$ elec.	Coupling constant calculated	Coupling constant observed
NH <sub>3</sub>	$\begin{array}{c} \text{H} \\   \\ \text{N}-\text{H} \\   \\ \text{H} \end{array}$	100	-0.40	-0.40	10.0	4.0 Mc	$\pm 4.10$ Mc
CH <sub>3</sub> CN	CH <sub>3</sub> -C $\equiv$ N	85	-0.50	-0.425	10.0	-4.25	-4.67
	CH <sub>3</sub> - $\overset{+}{\text{C}}=\text{N}^-$	5	0				
	$\overset{+}{\text{H}}\text{CH}_2=\text{C}=\text{N}^-$	10	0				
HCN	H-C $\equiv$ N	90	-0.50	-0.45	10.0	-4.5	-4.7
	H- $\overset{+}{\text{C}}=\text{N}^-$	10	0				
CH <sub>3</sub> NC	CH <sub>3</sub> -N=C:	5	+0.50	+0.025	10.0	+0.25	<0.5
	CH <sub>3</sub> - $\overset{+}{\text{N}}\equiv\text{C}^-$	95	0				
BrCN	Br-C $\equiv$ N	80	-0.50	-0.40	10.0	-4.0	-3.85
	$\overset{+}{\text{Br}}=\text{C}=\text{N}^-$	20	0				
NNO	$\text{N}=\text{N}=\text{O}$	45	0	-0.22	10.0	-2.2	-1.03
(end nitrogen)	$\text{N}=\text{N}^+-\text{O}^-$	55	-0.50				
NNO	$\text{N}=\text{N}=\text{O}$	45	0	0.0	10.0	0.0	-0.27
(central nitrogen)	$\text{N}=\text{N}^+-\text{O}^-$	55	0				

wave function,

$$\psi = a\{[\psi_{310}^{(1)}]_{\text{Cl}} + [\psi_{510}^{(1)}]_{\text{I}}\} \{[\psi_{310}^{(2)}]_{\text{Cl}} + [\psi_{510}^{(2)}]_{\text{I}}\}.$$

As long as the definition of ionic character given above is used, there is no great difference in the results with this type of wave function except in the way in which overlap effects appear, and again  $f \geq 0.20$ .

The method of treatment is probably too rough to allow an actual evaluation of the amount of hybridization from (13). This equation was developed, however, to show that overlap and other small effects obtained from a standard type of treatment are in the wrong direction to account for the discrepancy between the molecular and atomic coupling constants for Cl, hence  $s$ - $p$  hybridization is indicated.

The  $s$ - $p$  hybridization of the tetrahedral bonds of carbon is well recognized and produces orbitals which are one-quarter  $s$ , or with  $f=0.25$ . In addition, the "strongest" bond<sup>8</sup> using  $s$ - $p$  hybridization occurs when  $f=0.25$ . It has hitherto not been clear, however, whether the bond energy is sufficient to outweigh the energy required to displace some of the non-bonding electrons of an atom from the  $s$  orbit so that this orbit becomes available for bonding. In ICl apparently considerable  $s$ - $p$  hybridization occurs in the chlorine orbital, the bond possibly corresponding fairly closely to a tetrahedral carbon bond. Other molecules containing Cl which will be discussed below are consistent with

this conclusion. In addition,  $s$ - $p$  hybridization will be shown from a somewhat different and still clearer type of evidence to occur in nitrogen and arsenic, and presumably is rather common.

Before proceeding to other molecules, we shall review the assumptions involved in the conclusion that the chlorine bond is approximately a 20 percent-80 percent  $3s$ - $3p$  hybrid. Although chlorine is not a heavy atom, the measured atomic and molecular values of  $q$  are large enough that the effect of charges on the adjacent iodine atom is comparatively small, probably less than  $0.03q_{310}$ . Since the closed shells of electrons about the chlorine nucleus are inside of a valence shell of five electrons, they are very tightly bound and effects due to distortions of these shells are most probably less than  $0.01q_{310}$ . Electrons of the valence shell alone, then, are responsible for the observed quadrupole coupling. The fact that the molecular quadrupole coupling is 28 percent less than the atomic coupling and that the small effect of ionic character of the bond can account for only part of the discrepancy shows that either there is effectively more than one  $3p$  electron with  $m=0$  ( $s$ - $p$  hybridization), or that there are less than four  $3p$  electrons in the  $m=\pm 1$  states. Hybridization of the bonding orbital with any atomic orbit other than the  $3s$  would result in an increase rather than the observed decrease in the value of  $q$ . One is therefore forced into either  $s$ - $p$  hybridization or aban-

doing the assumption (made tentatively above) that the non-bonding  $p$  electrons remain essentially undisturbed. The latter choice seems much less likely because twice as many electrons must be removed from the  $m=1$  orbitals as have been added to the  $3p, m=0$  orbit to account for the observed effect. Although hybridization of the orbit of the bonding electron appears rather natural because of the advantage of increasing the bond energy, there would appear to be no good energetic reason for promoting a sizable fraction of an electron from the  $3p, m=\pm 1$  orbitals. In addition, the small amount of distortion and resulting quadrupole coupling for the case of non-bonding electrons in the alkali halides even in the presence of a strong electrostatic dipole affords good empirical evidence against the perturbation of the non-bonding  $p$  electrons in  $\text{ICl}$  to the extent needed to explain the observed effect.

#### MOLECULAR ELECTRONIC STRUCTURES DETERMINED FROM QUADRUPOLE COUPLING DATA

Rather than a detailed examination of each molecule such as has been given in  $\text{ICl}$ , we shall for the remainder of this discussion accept the general method of approximating  $q$ , and show how it may be rather simply applied to determine or verify the electronic structure of molecules from the measured quadrupole coupling constants. To correlate electronic structure and quadrupole coupling values we first describe the molecule as resonating between several structures or valence bond combinations and obtain the percentage importance of each structure from more or less standard types of evidence. For each structure the number of "unbalanced" electrons in  $p$  states around the nucleus in question is determined (a completely filled  $p$  shell containing six electrons has no unbalanced  $p$  electrons, a structure involving one bonding  $p_z$  orbital has one unbalanced  $p$  electron). Next the average number of unbalanced  $p$  electrons for the molecule—the weighted average of the values for the various resonant structures—is calculated. Finally, a value of the coupling constant per  $p$  electron is chosen to produce the best fit with the observed values for all molecules involving the same nucleus and the final "calculated" coupling constants obtained. In the two cases of  $\text{Cl}$  and  $\text{As}$  values of coupling constant per  $p$  electron are available from other types of data and these values are used.

For most nuclei values of the nuclear quadrupole moment are unknown and comparisons of measured and calculated values of  $q$ , of the sort made for chlorine in  $\text{ICl}$  in a previous section, cannot be carried out. It is still possible, however, to obtain information concerning the molecular electronic structure from the measured quadrupole coupling constants. If a value of the coupling constant for a single  $p$  electron is chosen to fit the measured values for the individual molecules, the

consistency of the assumptions involved in setting up the molecular electronic structures may be tested.

The contribution of the individual structures has been determined as far as possible from bond distances and the Pauling table of covalent radii as modified by Schomaker and Stevenson.<sup>14</sup> The modified radii for carbon and nitrogen suggested by Gordy<sup>15</sup> have also been accepted. Bond distances used are listed in Table IV. The contribution of ionic structures and structures involving atoms bearing formal charges has been calculated using the table correlating "partial ionic character" and differences in electronegativity given in Pauling's "Nature of the Chemical Bond" and to some extent dipole moment data. In a number of interesting cases modifications in these structures, suggested by a consideration of quadrupole coupling information, have been made.

Table V gives the structures of all molecules involving the halogens and arsenic whose quadrupole couplings are known. They have been chosen from a consideration of all structural information including nuclear quadrupole effects, and although differing in some cases from those proposed by earlier investigators, they appear just as consistent with previously available information. In addition, as shown in Table V, these structures give good agreement between measured and calculated quadrupole coupling constants, whereas some of the alternative proposals would give coupling constants in striking disagreement with the measured values. Data are given for only one isotope of each chemical element. While the individual isotopes of an element may have different values of the nuclear quadrupole moment, in the same molecule they will have identical values of  $q$  and therefore contribute no new information concerning the molecular electronic structure.

The halogen cyanides have been assumed to resonate between the structures  $\text{X}-\text{C}\equiv\text{N}$  and  $\text{X}^+=\text{C}=\text{N}^-$ . The percent contribution of each configuration has been determined from the observed internuclear distances and the table of covalent radii. Since the percentages obtained by using the  $\text{C}-\text{N}$  distance differs from that derived from the  $\text{C}-\text{X}$  distance, an average has been taken. The data on the percent contribution of individual valence bond structures calculated from independent bond distances for several molecules are given in Table IV. The discrepancies observable in this table as well as the difficulties pointed out below in bond lengths of the methyl halides indicate some lack of internal consistency in the table of covalent radii or their use with simple structural approximations. Since the calculation of bond distances from bond radii neglects a number of important considerations, this apparent lack of consistency—pointed out clearly by the rather accurate bond distances obtained from microwave spectra—is not surprising.

<sup>14</sup> V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.* **63**, 37 (1941).

<sup>15</sup> W. Gordy, *J. Chem. Phys.* **15**, 81 (1947).

A double bond involving one of the halogen atoms is assumed in Table V to consist of a  $\sigma$ -bond (in Mulliken's notation) of the same character (hybridized  $s$ - $p$  or pure  $p$ ) as the single bond to that atom and a  $\pi$ -bond of pure  $p$  character. A positive formal charge on an atom, since it pulls the electrons closer to the nucleus, is taken into account by multiplying the number of unbalanced  $p$  electrons by a factor 1.25 estimated from atomic fine structure. Similarly for a negative formal charge, a factor  $1/1.25$  is introduced.

The methyl halides, in Table V, have been considered as containing a single covalent bond between carbon and halogen, having some "ionic character." The problem of evaluating the ionic character of the carbon halogen bonds is somewhat difficult as can be seen in the case of the C—I bond in  $\text{CH}_3\text{I}$  which should have zero moment on the basis of the electronegativity differences and which has an observed bond moment of 1.2 Debye units. Complications such as interaction between the C—H and C—X bonds, as well as effect on electronegativity of possible hybridization,<sup>16</sup> are presumably responsible. Since the ionic character of the carbon-halogen cannot be correctly assigned from a simple consideration of the carbon-halogen electronegativity differences, the decision has been based on the dipole moment and the quadrupole data. These indicate 15–20 percent ionic character. It should perhaps be mentioned that this picture fails to account for the anomalous carbon halogen bond lengths in these molecules which are significantly greater than the covalent single bond radii. A shortening of the bond due to resonance with ionic states would generally be expected.

In the case of the sodium halides the quadrupole coupling constant is an especially sensitive indication of the amount of covalent character. From a consideration of the quadrupole coupling data, one can with some confidence assign a maximum of 4 percent covalent character in  $\text{NaCl}$  and 3 percent in  $\text{NaBr}$ . While these values are quite different from the figures which would have been chosen on the basis of electronegativity differences alone, they are of the same order of magnitude as the 5–10 percent figure quoted by Pauling<sup>17</sup> for alkali halide gas molecules based on a consideration of curves of energy *versus* internuclear distance for the ionic and covalent molecules. The observed dipole moment of gaseous cesium fluoride indicates only 60 percent ionic character if polarization is completely neglected. However, the quadrupole coupling constants give rather clear evidence that the alkali halides should be considered as almost purely ionic with a large amount of polarization responsible for reducing the dipole moment. This is in agreement with similar conclusions of Mulliken<sup>18</sup> from a study of the electronic spectra of these molecules.

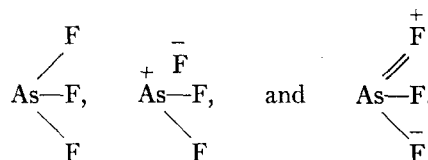
<sup>16</sup> R. S. Mulliken, *J. Chem. Phys.* **3**, 573 (1935).

<sup>17</sup> See reference 8, p. 46.

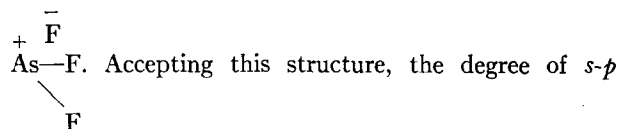
<sup>18</sup> R. S. Mulliken, *Phys. Rev.* **51**, 310 (1937).

Because the quadrupole coupling was known in the atomic case for  $\text{Cl}^{35}$ , it was shown above that  $s$ - $p$  hybridization occurs in the Cl bond and for this reason we have taken the pure covalent single Cl bond as of 82 percent  $p$ -character and used the value  $-110.4$  Mc obtained from atomic data for the coupling per  $p$  electron. In the cases of Br and I, although hybridization may be expected, the degree or character of hybridization is not yet known and we have assumed the covalent single bonds to involve pure  $p$  orbitals. This assumption does not introduce much error in the relative values of quadrupole couplings as long as the amount of hybridization of a single bond does not vary from molecule to molecule.

Possible structures considered for arsenic trifluoride were



Both the dipole moment and bond distance allow only negligible contributions from structures other than



Accepting this structure, the degree of  $s$ - $p$  hybridization can be estimated from the quadrupole coupling, since in this case the value of the quadrupole moment is known,<sup>19</sup> at least roughly, from atomic data to be  $0.3 \times 10^{-24} \text{ cm}^2$ . The resulting wave function for the bonding orbitals is of the form  $(\frac{1}{5})^{1/2} \psi_s + 2(\frac{4}{5})^{1/2} \psi_p$ . This wave function would not be very much changed if some importance is given the other two molecular structures mentioned above.

If the  $p$  orbitals of  $\text{AsF}_3$  were not hybridized, there would be a very small or zero coupling constant since the three perpendicular  $p$  orbits would be equally filled and produce a spherical charge distribution around the nucleus. Consider now the three  $p$  orbits of the valence shell referred to axes with  $z$  oriented along the molecular axis rather than any of the As—F bonds. If hybridization occurs and increases the angle between bonds to a value greater than  $90^\circ$  ( $100^\circ$  is the best available value of bond angle for  $\text{AsF}_3$ ), then a defect of electrons along the molecular axis might be expected since the  $p_z$  orbit oriented along this axis would not be as much occupied by bonding electrons as the  $p_x$  and  $p_y$  orbits perpendicular to the axis. However, if this hybridization is produced by use of the  $s$  orbit of the valence shell—and only in this case—the two non-bonding electrons of the valence shell must be promoted to an orbit which contains a  $p_z$  component. Since this non-bonding orbit contains two electrons whereas the bonding orbits

<sup>19</sup> H. Schuler and M. Marketu, *Zeits. f. Physik* **103**, 434 (1937).

contain on the average only one electron, there is an excess of electrons along the molecular axes instead of a defect. Such an excess is proved by the sign of the quadrupole coupling constant in  $\text{AsF}_3$ , showing definitely that the bonding orbitals are  $s$ - $p$  hybrids.

Thus as in the case of Cl, a considerable amount of  $s$  character is demanded in the As bonds. Together with the observed bond angle ( $100^\circ$ ), this indicates the correctness of Pauling's suggestion<sup>20</sup> that a compromise results between the tendency of the molecule to form the "strongest possible" bonds (tetrahedral bonds) and the tendency in the case of atoms with an unshared pair to keep the unshared pair in the lower energy orbital.

The approximations involved in the calculation of the quadrupole coupling constants are less valid for the case of the lighter nucleus, nitrogen, than for the halogens and arsenic. This is primarily because in a light atom the contribution to  $q$  of a  $p$  electron is large but not overwhelmingly large by comparison with other neglected effects. The data for molecules containing nitrogen have been collected in Table VI (a and b). Any conclusions drawn from these data must be somewhat more tentative than those presented in the preceding sections, both because of less accuracy in the approximations and because the double and triple bond structures characteristic of N are less well understood than are single bonds.

Most authors have discussed the nitrogen bonds in ammonia and related molecules in terms of pure  $p$  bonds with some ionic character.<sup>21</sup> If such structures were assumed in Table VI, however, the resulting coupling constants would all be uniformly very small or zero in contradiction to experiment. Consequently, in Table VI we have adopted the next least radical assumption—that the nitrogen bonds are  $s$ - $p$  hybrids. Nitrogen single bonding orbitals are assumed to have tetrahedral wave functions  $\psi = \frac{1}{2}\psi_s + (\sqrt{3}/2)\psi_p$ .

In Table VIa the  $\sigma$ -component of multiple bonds has been assigned a similar tetrahedral wave function ( $\frac{1}{2}\psi_s + (\sqrt{3}/2)\psi_p$ ) while in Table VIb calculations are presented for  $\sigma$ -wave functions of the form  $(\frac{1}{2})\psi_s + (\frac{1}{2})\psi_p$ . The  $\pi$ -components of multiple bonds are assumed to be pure  $p$  orbitals.

The amount of ionic character of the N—H bonds in ammonia has been calculated from electronegativity differences and the Pauling curve as 20 percent. The observed dipole moment would indicate 33 percent ionic character, but is considered less reliable. For HCN,  $\text{CH}_3\text{CN}$ , and  $\text{CH}_2\text{NC}$  the contributions of the various resonating structures were obtained from the values of bond distances. In  $\text{N}_2\text{O}$  not only do the contributions of the individual bond structures calculated from the two different bond distances fail to agree but one of them leads to a value of the dipole moment in

poor agreement with experiment. The structure suggested by the dipole moment (as well as one of the bond distances) gives approximately equal importance to the two structures listed in Table VIa. The relative importances 45 percent–55 percent are chosen to best fit the quadrupole coupling data.

For the nitrogen-containing molecules there are three possible sets of molecular electronic structures which might be consistent with the quadrupole coupling data. In the first of these a rather poor agreement (especially in the case of  $\text{N}_2\text{O}$ ) may be obtained by assuming less than 25 percent  $s$  character for the bond orbitals in ammonia and about 50 percent  $s$  character for the bonds in the other molecules. These are the bond types used in Table VIb. The poor fit to the experimental data and the relative implausibility of these assumptions tend to rule out this set of structures.

The second possibility, while yielding excellent agreement between calculated and observed coupling constants, involves the assumption of tetrahedral bonds for both single and multiple bonds in these nitrogen compounds. Penney<sup>22</sup> has presented calculations which argue against this picture of multiple bonds.

The structural assumptions used in Table VIa, while apparently rather plausible, lead to poor agreement with ammonia when tetrahedral bonding orbitals are assumed for the  $\text{NH}_3$  molecule. They lead to a quite satisfactory agreement when the following electronic structure roughly similar to that proposed by Mulliken<sup>23</sup> is adopted. Four molecular orbitals are set up; three bonding  $[\pi]^2[\pi]^2[z]^2$  and one non-bonding  $[s]^2$ . The two  $[\pi]$  orbitals are approximated in the immediate neighborhood of the N atom by nitrogen  $2p$  orbitals. The  $[z]$  orbital is assumed to possess 75 percent  $p$  character, while the  $[s]$  orbital is equivalent in the region near N to an orbital containing 25 percent  $p$  character and 75 percent  $s$  character. In assigning ionic character a figure of 20 percent was estimated as described above so that we have added  $\frac{1}{2}$  of an electron to each of the three bonding orbitals.

It is this structure which is designated in Table VIa as  $\text{N}\equiv\text{H}_3$  and which is considered most probable. It gives a quadrupole coupling for ammonia which is consistent with the nitrogen quadrupole couplings in other molecules assuming the usual picture for multiple bonds but with a hybridized component as discussed above. Such a structure for the nitrogen bonds in ammonia makes them closely similar to the nitrogen bonds in the  $\text{C}\equiv\text{N}$  group. This similarity is suggested directly by the observation that the quadrupole coupling constants for N in ammonia and in the cyanides are substantially the same. Since no other reasonable structure for  $\text{NH}_3$  seems to give the correct coupling constants, the electronic environments of N in  $\text{NH}_3$  and  $\text{C}\equiv\text{N}$  must be very similar.

<sup>20</sup> See reference 8, p. 87.

<sup>21</sup> E.g. W. C. Price, *Ann. Rep. Chem. Soc.* **36**, 50 (1939).

<sup>22</sup> W. G. Penney, *Proc. Roy. Soc.* **A144**, 166 (1934) and **A146**, 223 (1934).

<sup>23</sup> R. S. Mulliken, *J. Chem. Phys.* **3**, 506 (1935).

The small values of the coupling constants for N in methyl isocyanide and the inner N atom in  $N_2O$ , while casting no special light on the nature of the bonding orbitals, furnish new evidence of the correctness of the resonant structures involving quadrivalent nitrogen and of the correctness of the basic assumptions underlying the calculations of coupling constants.

It may be noted that very good agreement is obtained in Tables IV and VIa between "calculated" and measured coupling constants for all molecules for which quadrupole coupling data are at present available. The only known cases which are not listed and considered are some additional alkali halides which all show very small couplings just as do the alkali halides discussed here, and the nuclei  $S^{33}$ ,  $B^{10}$ , and  $B^{11}$ . In each of the latter three cases, a coupling constant in only one molecule has been obtained, and since in addition no atomic data on their quadrupole couplings are available for comparison, very little useful molecular information can be obtained by discussing them. The good agreement shown in Tables IV and VIa, using molecular electronic structures which are very reasonable in the light of other reliable evidence, is a satisfying argument for the correctness of the method and principles underlying the calculation of quadrupole coupling constants.

### SUMMARY

Thus, an examination of nuclear quadrupole couplings in molecules in terms of the approximate method discussed above leads to the following conclusions:

1. At least 15 percent hybridization of  $p$  bonding orbitals with  $s$  orbitals occurs in N, Cl, and As bonds and presumably is rather common in other elements.
2. The electronic structures of the three nitrogen bonds in ammonia is very similar to that of nitrogen in the  $-C\equiv N$  group.
3. Bonds of most of the alkali halides show less than 3 percent true covalent character, and the molecules should be considered primarily ionic with a considerable amount of polarization of each ion.

Further measurements of quadrupole coupling constants should afford additional useful tests of molecular structure.

Nuclear quadrupole moments may be approximated by combining the data of Tables V and VI on the quadrupole coupling per  $p$  electron with estimates of  $\partial^2 V/\partial z^2$  for a  $p$  electron in the atomic state. This yields the values given in Table VII and discussed in the appendix.

### APPENDIX

*Determination of nuclear quadrupole moments.*—The values given in Tables V–VI for quadrupole coupling per  $p$  electron may be used to evaluate nuclear quadrupole moments if the magnitude of  $\partial^2 V/\partial z^2$  produced at

the nucleus by a  $p$  electron is known. The latter quantity can be approximately obtained from expression (1) or (2).

For the halides,  $\partial^2 V/\partial z^2$  can be readily evaluated from expression (2) and has already been given above for F, Cl, and I as  $21 \times 10^{15}$ ,  $19.8 \times 10^{15}$ , and  $45 \times 10^{15}$  e.s.u., respectively. The values for  $\Delta\nu$  used for these elements are well known as 404, 881, and  $7603 \text{ cm}^{-1}$ . The numbers 49, 13, and 6 were taken for  $Z_i$ . For Br,  $\Delta\nu$  is  $3685 \text{ cm}^{-1}$  and if  $Z_i$  is taken as 31,  $\partial^2 V/\partial z^2 = 34 \times 10^{15}$  e.s.u. It must be remembered that the values

TABLE VII. Nuclear quadrupole moments derived from measured quadrupole coupling constants in molecules and approximate evaluation of  $\frac{\partial^2 V}{\partial z^2}$ .

Nuclei	Quadrupole moment	Ratio of moments
$N^{14}$	$\sim 0.02 \times 10^{-24} \text{ cm}^2$	
$S^{33}$	$\sim -0.08$	
$Cl^{35}$	$-0.077$	
$Cl^{35}/Cl^{37}$		1.27
$As^{75}$	0.3	
$Br^{79}$	0.28	
$Br^{79}/Br^{81}$		1.198
$I^{127}$	$-0.75$	

here are for the molecular case (or for an atomic case with  $m=0$ ), so that expression (2) must be multiplied by  $-2l/(2l-1)$  or  $-2$ . These values immediately allow determination of the Cl, Br, and I quadrupole moments as given in Table VII.

The  $Cl^{35}$  quadrupole moment given in Table VII is close to the true value  $-0.079 \times 10^{-24} \text{ cm}^2$  (cf. reference 13) because the true value was known and hybridization could be allowed for. A previous estimate<sup>5</sup> of the  $Cl^{35}$  quadrupole moment without allowing for hybridization was  $-0.067 \times 10^{-24} \text{ cm}^2$ . The estimated quadrupole moments of Br and I will also be too small if these atoms exhibit  $s-p$  hybridization, but too large if  $p-d$  hybridization occurs. At least in the case of the heavy atom I, some  $p-d$  hybridization is not unlikely, and may explain why the  $I^{127}$  quadrupole moment given in Table VII is larger than the approximate value  $-0.45 \pm 0.15 \times 10^{-24} \text{ cm}^2$  obtained from atomic spectra.<sup>24</sup>

Determination of  $\partial^2 V/\partial z^2$  for N requires a somewhat more lengthy procedure than did the halogens. Probably the most reliable and simplest estimate is obtained by noticing that for double ionized N,  $\Delta\nu = 174.5 \text{ cm}^{-1}$ , and that for quadruply ionized F,  $\Delta\nu = 746 \text{ cm}^{-1}$ , or just 1.85 times the value of  $\Delta\nu$  for neutral F. An equivalent  $\Delta\nu$  for neutral N for substitution in expression (2) may then be taken as  $174.5/[1+(0.85/2)] \text{ cm}^{-1}$ . If  $Z_i$  is assumed to be 4,  $\partial^2 V/\partial z^2 = 9.9 \times 10^{15}$  e.s.u. A similar, but less reliable, value can be obtained using formula (1) and estimating an effective value of  $n$  from the ionization potential of N. Using the value 24 Mc of Table VIa for the coupling constant per  $p$  electron, the  $N^{14}$

<sup>24</sup> K. Murakawa, Zeits. f. Phys. 114, 651 (1939).

quadrupole moment would be  $0.033 \times 10^{-24}$  cm<sup>2</sup>. However, using the value 9.0 Mc indicated by Table VIb, its quadrupole moment is  $0.012 \times 10^{-24}$  cm<sup>2</sup>. The value  $0.02 \times 10^{-24}$  cm<sup>2</sup> chosen for the table is thus seen to be more uncertain than are the halide quadrupole moments.

The quadrupole moment of As<sup>75</sup> given in Table VII represents no new determination because the structure of AsF<sub>3</sub>, the only molecule for which the As coupling constant is available, has been determined so that the coupling constant will give the correct, known As<sup>75</sup> quadrupole moment.

Evaluation of  $\partial^2 V / \partial z^2$  for S<sup>33</sup> is done in essentially the same way as for N<sup>14</sup>. For triply ionized S,  $\Delta\nu = 950.2$  cm<sup>-1</sup>. The ratio between for quadruply ionized Cl and singly ionized Cl is 1.70. An equivalent for neutral S is taken as  $950.2 / (1 + \frac{3}{4} \times 0.70)$  cm<sup>-1</sup>, and  $Z_i$  as 12.5. This yields  $\partial^2 V / \partial z^2 = 14.7 \times 10^{15}$  e.s.u. The structure of OCS, in which the S<sup>33</sup> coupling constant has been measured as -28.5 Mc, has not been discussed above. The molecule is assumed to resonate between the structures  $\text{O}=\text{C}=\text{S}$ ,  $\text{O}^--\text{C}^+\equiv\text{S}$ , and  $\text{O}^+\equiv\text{C}-\text{S}^-$ . A calculation

from bond distances gives importances of 58 percent, 14 percent, and 28 percent, respectively, to these three structures. Assuming the double and triple bonds are similar to those indicated for N in Table VIa, and that the single bond is a 25 percent-75 percent *s-p* hybrid, the calculated average fraction of unbalanced *p* electron is then 0.27, giving a quadrupole moment  $-0.098 \times 10^{-24}$  cm<sup>2</sup>. On the other hand, if all bonds involve pure *p* orbitals only, the calculated average fraction of unbalanced *p* electron is 0.52, giving a quadrupole moment  $-0.052 \times 10^{-24}$  cm<sup>2</sup>. The value  $-0.08 \times 10^{-24}$  cm<sup>2</sup> chosen for the table thus may involve considerable error because of uncertainty in the bond structure of OCS, but the sign appears to be definitely determined, and the magnitude is probably not in error by more than 50 percent. Measurement of the S<sup>33</sup> coupling in other molecules may allow a more accurate determination of its quadrupole moment.

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