

Halogen Nuclear Quadrupole Coupling Constants: Comparison of *ab initio* Calculations which include Correlation, with Experiment*

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Ab initio determination of the electric field gradient (EFG) tensors at halogen and other centres enabled determination of the nuclear quadrupole coupling constants (NQCC) for a diverse set of axially symmetric (C_{3v} , $C_{\infty v}$, $D_{\infty h}$ and other symmetries) inorganic and organic molecules, where the heavy elements are Cl, Br, and I with C, Si, Ge, and Sn hydrides. The latter elements are in an approximately tetrahedral environment. The study presents results at a standardised level of calculation, triple-zeta in the valence space (TZV) plus polarisation functions (TZVP) for the equilibrium geometry stage; all-electron MP2 correlation is included in all these studies. f-Orbital exponents were optimised for both Br and I centres in the methanes; the atomic populations of the f-orbital components are very small for the Br- and I-atoms, confirming their role as polarisation functions rather than having any bonding character. The EFG are determined at equilibrium with the TZVP basis set, except Sn and I centres where the basis set is TZV + MP2. For the bromo and iodo compounds, especially the latter, it is essential to allow for core polarisation, by decontraction of the p,d-functions. This is conveniently done by initial optimization of the structure with a partly contracted basis, followed by reestablishment of the equilibrium structure with the decontracted basis. A close correlation of the observed (microwave spectral) data with the calculations was observed, using the 'best' values for the atomic quadrupole moments for Cl, Br, and I; thus there seems no need to postulate that the value of Q_{Br} for ^{75}Br and ^{81}Br are in error. The SCF and MP2 wave-functions were converted into localised molecular orbitals by the Boys Method. This allowed a study of the differing s/p/d-hybridisation ratios, and the centroid positions, to be compared with the quadrupole coupling constants. The charge distributions for the atoms were converted into local bond dipoles, which in turn are correlated with the electronegativity differences of the bonded atoms.

1. Introduction and Background

Previously we have reported *ab initio* studies of a variety of organic and inorganic molecules, containing various quadrupolar nuclei, especially ^{14}N [1], $^{10,11}B$ [2], ^{33}S [3], and ^{17}O [4]; the present paper continues this survey to cover halogen quadrupole coupling, with particular reference to the stable isotopes of the halogens, chlorine, bromine and iodine. Both inorganic and organic molecules are reported, but in this paper we consider only axially symmetric molecules, i.e. those with one unique symmetry axis, such that the asymmetry parameter (η) is zero. In the normal convention for quadrupole coupling constants, $\chi_{zz} \geq \chi_{yy} \geq \chi_{xx}$, the further identities with the inertial axis data are $\chi_{zz} = \chi_{aa}$, $\chi_{yy} = \chi_{xx} = \chi_{bb} = \chi_{cc}$. In a later paper, we will consider the non-axial symmetry molecules, where $\eta \neq 0.0$ occurs.

NQR has been widely used for studies of halogenated

compounds, but because of the 3/2 and 5/2 nuclear spin, only the resonance frequencies (ν) can be determined from polycrystalline samples; the asymmetry parameter (η) requires the use of a single crystal or other techniques, [5]. As a typical example, the ^{35}Cl NQR frequency for methyl chloride at 77 K is 34.029 MHz, to be compared with 37.3767 MHz for the vapour by MW study at room temperature [6][7]. The effect is both one of temperature, and lattice effects. Indeed, analysis of the NQR frequency and molar heat capacity against temperature lead to the value of $-2.870(330)$ MHz as the crystalline contribution to the observed frequency at 0 K [8].

2. Theoretical Studies

We have previously classified our studies into three types: (a) studies of individual molecules at equilibrium; (b) similar studies of small clusters of molecules, where a test molecule is surrounded by its nearest shell of neighbours from the crystal lattice; (c) lattice calculations where the calculation is carried out in the unit cells struc-

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ture of the crystal. The present work is concerned with method (a). Microwave spectroscopy (MW) for gaseous molecules leads to data directly comparable with the present results. The inertial axes are a result purely of the set of atomic masses, and are not connected with the equilibrium structure and its electronic wave-function except via the atomic numbers of the nuclei.

Our methods of study involve *ab initio* calculation of the electric field gradients (EFGs) (q_{ij}) at the centre of interest in the molecule, and conversion to the nuclear quadrupole coupling constants (NQCCs) (χ_{ii}), by means of (1) and (2). All total contributions are made up of sums of electronic and nuclear terms [9], and the former of these is itself made up of sums from doubly occupied molecular orbits (MOs) (SCF calculations), i.e., the term for the orbital in question is multiplied by 2 electrons; in the case of the MP2 calculations, the orbital value is multiplied by the occupation number, and summed over all the Natural Orbitals (NOs) of the calculation. In (1), the SCF or MP2 wave-function is denoted by ψ_0 .

Typical diagonal and off-diagonal EFG Operators:

$$\begin{aligned} q_{zz} &= \langle \psi_0 | (3z^2 - r^2) / r^5 | \psi_0 \rangle, \\ q_{xy} &= \langle \psi_0 | (3xy) / r^5 | \psi_0 \rangle. \end{aligned} \quad (1)$$

NQCC and EFG:

$$\chi_{ii} = e^2 Q_Z q_{ii} / h = 234.96 Q_Z q_{ii}. \quad (2)$$

Although not central to this study, we note that in Mössbauer spectroscopy the Quadrupole Splitting (QS), in ^{119}Sn for example, which is relevant here, is given by $(1/2)e^2 Qq$ above [10]. There have been a number of previous *ab initio* studies of halogen nuclear quadrupole coupling, as well as empirical studies which are summarised by Lucken [5]. Relevant more recent studies can be summarised as follows: semiempirical [11, 12], *ab initio*, [13, 14], pseudopotential studies on molecules (structures only) with H_3MX where the central atoms include the series $\text{X} = \text{C, Si, Ge, Sn}$, and the halides are $\text{X} = \text{F, Cl, Br, I}$ [15], and inorganic species such as bromine chloride [16–18]. None of these more recent individual studies have either the range or depth of the present investigation, but will be referred to when individual comparisons with experiment are made.

2.1. The Present Theoretical Study

The first stage is determination of the equilibrium structure and the corresponding inertial axis system, and comparison with experiment. In the present paper we do

not discuss the equilibrium structures in great detail, but since all molecular properties such as NQCC are evaluated at the equilibrium structure, and total energies give a measure of the calculation overall quality relevant to previous work, we give a summary of the equilibrium structure geometric parameters and total energies in Tables 1 to 5. We are primarily concerned with the halogen atoms being connected to a tetravalent centre in the present study. The central atoms adjacent to the halogens are H, C and Si in most cases, but some simple Ge and Sn halides are also reported. While Sn has no quadrupolar stable isotopes, the ^{119m}Sn nucleus is commonly observed in Mössbauer spectroscopy. The simple germyl and stannyl halides give information to compare with experiment at the central atoms. Some studies of germyl chloride gave no ^{73}Ge isotope (7.8%) quadrupolar splitting [19, 20], but more recent MW studies have observed the natural abundance ^{73}Ge splitting as well as the $^{35,37}\text{Cl}$ splitting [21].

2.2. Basis Sets

The Huzinaga/Dunning triple zeta valence (TZV) type [22] was extended by polarisation functions [23]; some other larger elements were from our own bases, and are described more fully in [24, 25]. However, it was found that, while the bromine and iodine bases of Huzinaga [26, 27] with total functions $14s11p5d$ (Br) contracted to s/p/d terms [61111111/611111/411], and $18s14p8d$ (I) contracted to [3322212111/3332111/4211], respectively, led to very acceptable structural parameters, this was not true of the quadrupole coupling at ^{127}I in particular, with $^{79,81}\text{Br}$ being only marginally acceptable. It was necessary to decontract the bromine p-functions further to [311111111]. The iodine basis above required the addition of further terms of each of s,p,d-type, the p-set becoming [321111111111]; if this was not done, then HI had the dipole reversed from the expected direction. Finally, the f-orbital exponents for Br and I were optimised, by total energy lowering, for the bromo- and iodo-methanes. The final f-orbital exponents were 2.75 (I) and 7.02 (Br); these values are discussed further below. The germanium basis set was similarly chosen by adaption of the above atomic data [27] to yield s/p/d terms [3111111111/2111111111/2111]. Finally, the tin basis set, also derived from Huzinaga [27], was (18s/14p/8d) decontracted from an initial [3322212111/33311111/311111] to [3311111112111/311111111111/311111] for the final EFG studies. For Sn, the Huzinaga atomic basis is unsatisfactory since two s-exponents are nearly

identical (0.548 and 0.497), causing problems with linear dependence unless the former is taken in linear combination with another term, which was the course adopted here.

The derivation of basis sets for high atomic number atoms, where few bases exist, can be expedited by the little-used fact that atomic orbital exponents vary with the square of the atomic number (Z). Hence given the availability of large bases for smaller atoms, atomic bases for large atoms can be constructed by scaling the small atom bases by $(Z/Z')^2$, to within 1% of the energy optimized values. The d/f-orbital exponents may need to be selected by analogy with the corresponding s,p-bases in these circumstances. We have used this procedure to generate large bases for Ge, Sn and Pb from Si bases.

As a further check on the role of the f-orbitals in iodomethane, we performed a further optimisation of the structure at the MP2 level, with a Cartesian set of d-orbital functions at the C-I mid-point. The angular terms from a mid-bond d-orbital mimic an atom-centred f-orbital.

In summary, the equilibrium geometries were obtained with the semi-contracted sets shown above; the equilibrium geometries were then re-established with the full decontracted sets, and the wave-functions saved as NO. It was necessary to reoperate the optimization mode for the latter, since otherwise the NO are not stored by the programme. In principle, it is possible to perform the LMO calculations on the NO's by either performing the localisation followed by MP2, or the MP2 followed by LMO; in the present study the former process was performed, but in practice, the MP2 effects are relatively small, as is usual with saturated compounds, allowing the SCF and MP2 data to correlate closely. All of the calculations were performed with the GAMESS-UK quantum chemistry package [28, 29].

3. Atomic Quadrupole Moments

The present set of nuclei has nuclear spin $I = 3/2$ (^{35}Cl , ^{37}Cl , ^{79}Br , and ^{81}Br), $I = 5/2$ (^{127}I) $I = 9/2$ (^{73}Ge). The individual atomic quadrupole coupling constants, with standard deviations in parentheses, for ^{35}Cl ($-81.65 \text{ mb}(80)$) and ^{37}Cl ($-64.35 \text{ mb}(64)$) [30] are relatively well determined, and their ratio is known with great accuracy (1.268877) [31]. These values, and the less well determined values [32] for the ^{79}Br and ^{81}Br , ^{127}I , and ^{73}Ge isotopes have Q_Z +331(4), +276(4), -789 and -173 mb, respectively. The excited state ^{119m}Sn quadrupole moment ($I = 3/2$) is not known with confidence; the long-standing value for Q_{Sn} is -61 mb [33], but more recent studies suggest a much higher value of $128 \pm 7 \text{ mb}$ [34]. This latest value is based on the (very satisfactory) linear regression of calculated EFG (FP-LMTO method) against experimental Mössbauer quadrupole splittings. The key question is whether this method returns all of the core orbital contributions to the EFG. If not, then the effective Q_{Sn} will be artificially high. These values will be used for conversion of electric field gradients (EFG/a.u.) to quadrupole coupling constants (NQCC/MHz) via (2), in the present work. The EFG to NQCC conversion ratios are: ^{35}Cl : 1 a.u. = -19.184484 MHz ; ^{79}Br : 1 a.u. = 77.77176 MHz ; ^{127}I : 1 a.u. = -185.38344 MHz ; ^{73}Ge : 1 a.u. = -40.64808 MHz ; ^{119m}Sn : 1 a.u. = -14.33256 MHz ; ^2H : 1 a.u. = 671.9856 kHz .

Table 1. Equilibrium Total Energies (a.u.) for Compounds Studied.

| Compound | Energy | Compound | Energy |
|-------------------------------------|--------------|---|--------------|
| HF | -100.30043 | HCl | -460.29694 |
| BH _r | -2573.24935 | HI | -6915.86945 |
| HBr(ext) | -2573.24935 | HI(ext) | -6917.07513 |
| HI(forbs) | -6917.30478 | | |
| F ₂ | -199.21973 | Cl ₂ | -919.35750 |
| Br ₂ | -5145.29597 | I ₂ | -13830.54293 |
| ClF | -599.30811 | BrF | -2672.28233 |
| IF | -7014.93742 | BrCl | -3032.32711 |
| ICl | -7374.96193 | IBr | -9487.93214 |
| Br ₂ (ext) | -5145.81491 | I ₂ (ext) | -13833.07624 |
| BrCl(ext) | -3032.58654 | BrF(ext) | -2672.54168 |
| IF(ext) | -7014.93742 | ICl(ext) | -7376.24458 |
| IBr(ext) | -9489.47445 | | |
| ClF ₅ (C _{4v}) | -957.76359 | IF ₅ (ext)(C _{4v}) | -7414.80095 |
| MeCl | -499.50021 | MeI | -6955.08455 |
| MeBr | -2612.45590 | MeI(diff) | -6956.48636 |
| MeBr(ext) | -2612.71545 | MeI(forbs) | -6956.73517 |
| MeBr(forbs) | -2612.95661 | CF ₃ Cl | -796.82583 |
| CF ₃ Br | -2910.03527 | CF ₃ I | 7253.80134 |
| SiH ₃ Cl | -750.65672 | SiH ₃ Br | -2863.60943 |
| SiH ₃ Br(ext) | -2863.86902 | SiH ₃ I | -7206.21946 |
| SiF ₃ Cl | -1048.81999 | SiF ₃ I | 7505.04500 |
| GeH ₃ F | -2177.63441 | GeH ₃ Cl | -2537.63902 |
| GeH ₃ F(diff) | -2177.65866 | GeH ₃ Cl(diff) | -2537.66720 |
| GeH ₃ Br(ext) | -4650.85715 | GeH ₃ I(ext) | -8994.40708 |
| GeH ₃ Br(diff) | -4650.88337 | GeH ₃ I(diff) | -8996.39748 |
| SnH ₃ Cl(diff) | -6445.98046 | SnH ₃ Br(diff) | -8559.17079 |
| SnH ₃ I(ext) | -12904.63026 | | |
| CIC≡CH | -536.24770 | BrC≡CH | -2649.20350 |
| IC≡CH | -6991.84543 | CIC≡CF | -635.31997 |
| BrC≡CF | -2748.27652 | IC≡CF | -7093.90301 |
| CIC≡CCF ₃ | -872.78877 | CIC≡CBr | -3108.56072 |
| BrC≡CH(ext) | -2649.46280 | BrC≡CF(ext) | -2748.27652 |
| IC≡CH(ext) | -6993.12553 | | |

4. Results and Discussion

The total energies for a range of hydrogen, alkyl, silyl, germyl and stannyl halides, using the bases described above, are given in Table 1. Equilibrium structures are in Table 2. The results obtained with the extended and diffuse bases for iodomethane are shown in Tables 3 and 4; these show the very large differences in MO contribution from the core and valence orbitals. The prin-

cipal EFG results and a comparison with experimental data for these axially symmetric compounds is shown in Tables 5 and 6; these data include both organic and inorganic compounds. The extended basis sets for the core orbitals of bromo- and germyl-compounds (ext) were utilised. Similar extension of the bases for iodine and tin was done, but additional more diffuse valence type AO's were added to be Huzinaga bases noted as diffuse, having exponents in the range 0.25–0.03; these contrast with

Table 2. Equilibrium Structures for Halides and Interhalogens.

| | | | | | |
|---------------------|--------------|------|-------------|-----|---------------|
| HCl | 1.27654 | HBr | 1.40994 | HI | 1.57441 |
| ClF | 1.6712 | BrF | 1.798 | ICl | 2.347 |
| IF | 2.492 | BrCl | 2.169 | IBr | 2.492 |
| MeCl | 1.7909(CCl) | | 1.0821(CH) | | 108.58(HCl) |
| MeBr | 1.9462(CBr) | | 1.0813(CH) | | 107.89(HBr) |
| MeI | 2.0943(Cl) | | 1.0808(CH) | | 109.30(HCl) |
| CF ₃ Br | 1.9361(CBr) | | 1.3279(CF) | | 110.2(FCBr) |
| CF ₃ I | 2.1536(Cl) | | 1.3316(CF) | | 110.64(FCI) |
| SiH ₃ Cl | 2.0679(SiCl) | | 1.4685(SiH) | | 108.33(HSiCl) |
| SiH ₃ Br | 2.2360(SiBr) | | 1.4689(SiH) | | 108.35(HSiBr) |
| SiH ₃ I | 2.4242(SiI) | | 1.4690(SiH) | | 108.75(HSiI) |
| SiF ₃ Cl | 2.0078(SiCl) | | 1.5863(SiF) | | 110.49(FSiCl) |
| SiF ₃ Br | 2.1736(SiBr) | | 1.5879(SiF) | | 110.71(FSiBr) |

Table 4. Methyl Iodide EFG Valence and Total Contributions.

| Basis | | q_{xx} | q_{yy} | q_{zz} |
|----------|------------|-------------|-------------|-------------|
| Standard | Nuclear | 0.116 | 0.116 | -0.231 |
| Standard | Electronic | 3.703 | 3.703 | -7.641 |
| Standard | Total | 3.819 | 3.819 | -7.641 |
| Extended | Nuclear | 0.116 | 0.116 | -0.231 |
| Extended | Electronic | 5.402 | 5.402 | -10.807 |
| Extended | Total | 5.518 | 5.518 | -11.038 |
| Extended | Total | χ_{xx} | χ_{yy} | χ_{zz} |
| Total | MHz | +1022.859 | +1022.859 | -2045.717 |

Table 3. Methyl Iodide Extended Basis Set EFG contributions by MO.

| Type | MO | Energy | q_{xx} | q_{yy} | q_{zz} | q_{zy} |
|-----------------|----|----------|-----------|-----------|-----------|----------|
| 1s _I | 1 | -1176.91 | 0.049 | 0.049 | -0.099 | |
| 2s _I | 2 | -180.78 | -0.142 | -0.142 | 0.284 | |
| 2p _I | 3 | -169.45 | 2823.655 | -1411.828 | -1411.828 | |
| 2p _I | 4 | -169.45 | -1411.828 | 2823.655 | -1411.828 | |
| 2p _I | 5 | -169.45 | -1418.291 | -1418.291 | 2836.582 | |
| 3s _I | 6 | -38.07 | -0.619 | -0.619 | 1.238 | |
| 3p _I | 7 | -33.22 | -769.811 | 1539.603 | -769.792 | |
| 3p _I | 8 | -33.22 | 1539.602 | -769.792 | -769.984 | |
| 3p _I | 9 | -33.22 | -769.984 | -769.984 | 1539.968 | |
| 3d _I | 10 | -24.30 | 36.382 | 36.313 | -72.696 | 2.704 |
| 3d _I | 11 | -24.30 | 36.314 | 36.382 | -72.696 | -2.704 |
| 3d _I | 12 | -24.30 | 36.821 | -73.095 | 36.273 | -2.716 |
| 3d _I | 13 | -24.30 | -73.095 | 36.821 | 36.273 | 2.716 |
| 3d _I | 14 | -24.30 | -38.805 | -38.805 | 77.610 | |
| 1s _C | 15 | -11.27 | -0.017 | -0.017 | 0.034 | |
| 4s _I | 16 | -7.30 | -1.363 | -1.363 | 2.726 | |
| 4p _I | 17 | -5.46 | 379.859 | -189.923 | -189.936 | |
| 4p _I | 18 | -5.45 | -189.936 | 379.859 | -189.936 | |
| 4p _I | 19 | -5.45 | -183.073 | -183.073 | 366.923 | |
| 4d _I | 20 | -2.40 | 14.575 | 14.460 | -29.215 | -1.679 |
| 4d _I | 21 | -2.39 | 14.640 | 14.640 | -29.215 | 1.679 |
| 4d _I | 22 | -2.39 | -28.931 | 14.550 | 14.381 | 1.667 |
| 4d _I | 23 | -2.38 | 14.550 | -28.931 | 14.381 | -1.667 |
| 4d _I | 24 | -2.38 | -14.695 | -14.694 | 29.390 | |
| Valence | 25 | -1.00 | -0.080 | -0.080 | 0.160 | |
| Valence | 26 | -0.80 | -12.117 | 24.231 | -12.113 | |
| Valence | 27 | -0.61 | 24.231 | -12.117 | -12.113 | |
| Valence | 28 | -0.61 | -0.208 | -0.208 | 0.417 | |
| Valence | 29 | -0.47 | -0.192 | 0.332 | -0.141 | |
| Valence | 30 | -0.36 | 0.332 | -0.192 | -0.141 | |
| Valence | 31 | -0.36 | -5.095 | -5.095 | 10.190 | |

Table 5. Electric Field Gradients (a.u.) at equilibrium.

| Compound | Centre | q_{zz} | Compound | Centre | q_{zz} |
|---------------------|--------|----------|----------------------|--------|----------|
| HF | F | -2.7106 | IF | F | -3.1774 |
| BrF | F | -3.8990 | CIF | F | -4.3536 |
| F_2 | F | -6.2092 | | | |
| HF | H | -0.5879 | HCl | H | -0.3151 |
| HBr | H | -0.2606 | HI | H | -0.2281 |
| HCl | Cl | -3.3557 | | | |
| CIF | Cl | -7.1206 | Cl_2 | Cl | -5.6191 |
| BrCl | Cl | -5.1904 | BrCl(ext) | Cl | -5.1978 |
| ICl | Cl | -4.3935 | ICl(ext) | Cl | -4.4461 |
| HBr | Br | -7.0443 | HBr(ext) | Br | -7.1753 |
| IBr | Br | -9.1872 | IBr(ext) | Br | -9.3906 |
| Br_2 | Br | -10.8999 | Br_2 (ext) | Br | -11.0052 |
| BrF | Br | -14.4243 | BrF(ext) | Br | -14.5406 |
| BrCl | Br | -11.7223 | BrCl(ext) | Br | -11.8169 |
| HI | I | -7.1100 | HI(ext) | I | -10.2131 |
| IF | I | -13.6098 | IF(ext) | I | -19.5498 |
| ICl | I | -11.9101 | ICl(ext) | I | -16.9802 |
| IBr | I | -11.2805 | IBr(ext) | I | -16.0835 |
| I_2 | I | -10.1438 | I_2 (ext) | I | -14.3463 |
| $ClC\equiv CH$ | Cl | -3.9530 | $ClC\equiv CH$ | H | -0.3615 |
| $BrC\equiv CH$ | Br | -8.4661 | $BrC\equiv CH$ | H | -0.3602 |
| $BrC\equiv CF$ | Br | -8.8315 | | | |
| $IC\equiv CH$ | I | -8.5431 | $IC\equiv CH$ | H | -0.2607 |
| $IC\equiv CH$ (ext) | I | -12.4227 | $BrC\equiv CH$ (ext) | Br | -8.6779 |
| $BrC\equiv CF$ | Br | -8.8325 | $BrC\equiv CF$ (ext) | Br | -9.0500 |
| $ClC\equiv CF$ | Cl | -4.1327 | $CF_3CC\equiv CCl$ | Cl | -3.9682 |
| MeCl | Cl | -3.7081 | SiH_3Cl | Cl | -2.0648 |
| MeBr | Br | -7.7065 | SiH_3Br | Br | -4.5806 |
| MeI | I | -7.6408 | SiH_3I | I | -5.1199 |
| MeBr(ext) | Br | -7.8228 | SiH_3Br | Br | -4.6585 |
| MeI(ext) | I | -11.0384 | SiH_3I | I | -7.3766 |
| CF_3Cl | Cl | -3.8408 | SiH_3Cl | Cl | -2.1044 |
| SiH_3Cl | Cl | -2.0648 | SiH_3Br | Br | -4.6585 |
| SiH_3I | I | -7.3766 | SiH_3F | Ge | -2.2530 |
| GeH_3F (diffuse) | Ge | -2.2338 | | | |
| GeH_3Cl (diffuse) | Cl | -2.3741 | GeH_3Cl (diffuse) | Ge | -2.1209 |
| GeH_3Br (diffuse) | Br | -5.1634 | GeH_3Br (diffuse) | Ge | -2.1347 |
| GeH_3I (diffuse) | I | -7.1968 | GeH_3I (diffuse) | Ge | -2.0481 |
| SnH_3Cl (diffuse) | Cl | -2.5682 | SnH_3Cl (diffuse) | Sn | -4.2531 |
| SnH_3Br (diffuse) | Br | -5.1164 | SnH_3Br (diffuse) | Sn | -3.1107 |
| SnH_3I | I | -8.4793 | SnH_3I | Sn | -3.6902 |

Rydberg functions which are one or more orders of magnitude smaller. The principal effect of these diffuse functions is to act like polarisation functions, but also to offer variational flexibility to the valence functions; thus a small shift of density moves from higher exponent functions to those further away from the nuclei. The effect of this is to modify the atomic populations slightly, and to slightly reduce the EFG at the centres in question. The charge distributions, as determined by Mulliken analyses of the wave-functions, are shown in Table 7, with the localised MO s,p,d-analyses of selected molecules shown in Table 8, with the centroid positions in Tables 9 and 10.

4.1. The f-Orbital Contributions in Iodo-Compounds

In the same way that Cartesian d-functions (X^2 , Y^2 , Z^2 , XY , XZ , YZ) contain an implicit s-function via the $X^2 + Y^2 + Z^2$ term. Cartesian f-functions have an implicit p-function through the term $X^2Y + Y^2Z + Z^2Y$ and related terms. Hence, such combinations could be important in the EFG of large halogens, where the p-orbitals are critical. Thus an investigation of the density of f-orbitals for I in particular is important. The optimised f-orbital exponents for I (2.75) and Br (7.02) are clearly higher than valence shell exponents, showing the polarisation

Table 6. Derived NQCC (MHz) and Comparison with Experiment.

| Compound | Centre | Calc. χ_{zz} | Obs. χ_{zz} | Ref. |
|------------------------|--------|-------------------|------------------|----------|
| ClF ₅ | Cl | -29.091 | -34.63(6) | [38] |
| SiH ₃ Cl | Cl | -39.612 | -39.70 | [39] |
| SiF ₃ Cl | Cl | -40.372 | -39.83(16) | [40] |
| GeH ₃ Cl | Cl | -46.479 | -46.9500(26) | [21] |
| HCl | Cl | -64.376 | -67.4605 | [41] |
| MeCl | Cl | -71.138 | -74.753 | [42] |
| HC≡CCl | Cl | -75.836 | -79.7358 | [43] |
| CF ₃ CC≡CCl | Cl | -76.129 | -79.4(30) | [44] |
| FC≡CCl | Cl | -79.285 | -83.0 | [45] |
| ICl | Cl | -85.295 | -85.8 | [46, 47] |
| BrCl | Cl | -99.717 | -102.378 | [16] |
| Cl ₂ | Cl | -107.799 | -115.0 | [48] |
| CIF | Cl | -136.606 | -145.87182 | [49] |
| SiH ₃ Br | Br | +362.301 | +334.981 | [50] |
| GeH ₃ Br | Br | +403.438 | +384(2) | [51] |
| HBr | Br | +558.033 | +532.23977 | [52] |
| MeBr | Br | +608.389 | +577.143 | [53] |
| CF ₃ Br | Br | +643.167 | +618.2(3) | [36] |
| BrC≡CH | Br | +674.892 | +648.113 | [54] |
| BrC≡CF | Br | +686.842 | +672.6 | [55] |
| Br ₂ | Br | +855.895 | +810.0 | [56] |
| BrCl | Br | +919.023 | +875.078 | [16] |
| BrF | Br | +1130.850 | +1086.89197 | [57] |
| IF ₅ I | I | -1179.890 | -1069.07(40) | [58] |
| SiH ₃ I | I | -1367.496 | -1245.1 | [59] |
| GeH ₃ I | I | -1512.123 | -1381(4) | [51] |
| HI | I | -1893.341 | -1828.059 | [60] |
| MeI | I | -2046.327 | -1934.136 | [37] |
| MeI (diffuse) | I | -1922.919 | -1934.136 | [37] |
| HC≡Cl | I | -2302.963 | -2254.1785 | [61] |
| I ₂ | I | -2659.563 | -2452.5837 | [62] |
| IBr | I | -2981.607 | -2731.0 | [63] |
| ICl | I | -3147.839 | -2929.0 | [46, 47] |
| IF | I | -3624.209 | -3440.748 | [64] |
| GeH ₃ F | Ge | -91.581 | -93.03(10) | [65] |
| GeH ₃ Cl | Ge | -89.576 | -93.0320(152) | [21] |

nature of the f-orbitals. Further, the atomic populations are very low; using the optimal f-orbital exponent on I in CH₃I, the total f-orbital population is 0.0662 electrons spread over 10 GTOs in 31 MOs, with a largest value of 0.0086e. Similarly, in CH₃Br the total and maximum values were 0.0155e and 0.0015e. Hence, given that the EFG is built up from the product of MO density terms and the intrinsic value for the MO (or NO), the f-orbitals must play a small, or even negligible role in these approximately tetrahedral molecules with singly bonded halogen, and will not materially effect the general conclusions. As a further check on the role of the f-orbitals in iodomethane, we performed a further optimisation of the structure at the MP2 level, with a Cartesian set of d-orbital functions at the C-I mid-point. The angular terms from a mid-bond d-orbital mimic an atom-centred f-orbital; the results are consistent with this and small in magnitude. The optimised d-exponent was 0.28, and at this

value the corresponding d-atomic populations of the terms were: r^2 -0.15096, $x^2 - y^2$ 0.0351, $z^2 - r^2$ 0.0182, $xy = yz = 0.0036$, xz 0.0097e, respectively. The r^2 term is merely replacing some of the s-orbital density, while all the other small values relate to those found with the Cartesian f-orbitals centred on the I atom. The effects are hence consistent but small in magnitude.

The present MP2 code in GAMESS-UK is limited to s,p,d-functions in the EFG evaluation module (a limitation shortly to be removed), but there is no reason to expect the f-orbital contributions to make a change to the conclusions here presented. Indeed, although in Table 1, it is clear that addition of f-orbitals (denoted 'forbs') to I in HI and MeI have a significant energy lowering effect, there is little effect on the equilibrium geometry, and the energy lowering is mostly recovered by extending the s,p,d-basis with additional diffuse functions (denoted 'diff'). In the final correlations with experiment, we use the most expanded basis ('diff').

4.2. Equilibrium and Localised Orbital Structures

The general level of agreement between the present equilibrium structures and those determined by MW spectroscopy is very good. Values are quoted for the present work to the accuracy which is claimed from experiment. Typical agreement for hydrogen halides and interhalogens are experimental values for HCl 1.27455, HBr 1.41460, HCl 1.6281 Å [35]. Values which are not so close are CIF and BrF (expt. 1.6281 and 1.759 Å). With the halogeno-methanes and -silanes, the same general level of accuracy and trends in series occur as from the MW determinations; thus for bromotrifluoromethane, the experimental data, C-F 1.3265(23), C-Br 1.9234(31) Å [36] are very similar to the present data. One small difference which is general, is the trend in angles HCX for CH₃X: Cl > Br > I; the present order is I > Cl > Br, but the effects are small. In general, the bond-length differences for chloro to bromo to iodo, in the series C-X and Si-X are about 0.15 Å in each case, in agreement with experiment. Since this is not central to the present subject, we do not pursue this further.

The localised MO's (LMO) for the present set of molecules show the following characteristics: (a) for the hydrogen halides and dihalogens we obtain one σ -bond and three lone pair orbitals in an approximately tetrahedral arrangement. (b) For the dihalogens, the LMO's adopt an ethane-like arrangement with staggered lone pairs (LP_X). (c) In the methyl and silyl halides the same stag-

Table 7. Mulliken Atomic Populations at equilibrium structure.

| | | | |
|-----------------------|------------|------------|------------------------------|
| HF | H 0.6384 | F 9.3617 | |
| HCl | H 0.7954 | Cl 17.2046 | |
| HBr | H 0.8272 | Br 35.1728 | |
| HI | H 1.0310 | I 52.9690 | |
| HI(forbs) | H 1.0160 | I 52.9840 | |
| CIF | Cl 16.7821 | F 92179 | |
| BrF | Br 34.7311 | F 9.2689 | |
| IF | I 52.5190 | F 9.4810 | |
| BrCl | Br 34.9816 | Cl 17.0184 | |
| ICl | I 52.7087 | Cl 17.2913 | |
| IBr | I 52.7070 | Br 35.2390 | |
| MeCl | Cl 17.1317 | C 6.3313 | H 0.8457 |
| MeBr | Br 35.1337 | C 6.3370 | H 0.8431 |
| MeI | I 52.8909 | C 6.6445 | H 0.8216 |
| MeI(forbs) | I 52.8979 | C 6.6411 | H 0.8204 |
| ClC≡CH | Cl 16.9764 | C 6.0229 | C 6.1892 H 0.8115 |
| BrC≡CH | Br 34.9292 | C 5.9884 | C 6.2683 H 0.8141 |
| IC≡CH | I 52.6859 | C 6.3038 | C 6.1872 H 0.8232 |
| FC≡CBr | F 9.1283 | C 5.8913 | C 6.0586 Br 34.9218 |
| FC≡CCl | F 9.1302 | C 5.8090 | C 6.0862 Cl 16.9746 |
| F ₃ CC≡CCl | F 9.1586 | C 5.4835 | C 6.0385 C 6.0677 Cl 16.9345 |
| H ₃ SiCl | H 1.1020 | Si 13.4083 | Cl 17.2857 |
| H ₃ SiBr | H 1.0962 | Si 13.4142 | Br 35.2974 |
| H ₃ SiI | H 10.813 | Si 13.7072 | I 53.0488 |
| H ₃ GeCl | H 1.1250 | Ge 31.2038 | Cl 17.4212 |
| H ₃ GeBr | H 1.1201 | Ge 31.2011 | Br 35.4387 |
| H ₃ GeI | H 1.1024 | Ge 31.5404 | I 53.1523 |
| H ₃ SnCl | H 1.1250 | Sn 49.2038 | Cl 17.4212 |
| H ₃ SnBr | H 1.1043 | Sn 49.2862 | Br 35.4010 |
| H ₃ SnI | H 1.1024 | Sn 49. | I 53. |

gered electron-pair arrangements occur, while the trifluoro-methanes and -silanes have similar near tetrahedral XF bond LMO's, while the LP_F on any F have lone-pairs facing the opposite pair of F-atoms.

4.3. EFG and Derived Quadrupole Coupling Constants in Relation to Experiment

4.3.1. Core Relaxation in the Iodo- and Bromo-Compounds

First we note the basis set effect for the Br and I halogens. The example shown is methyl iodide, where we show the contribution from each MO to the EFG. The molecules lies along the z-axis. Although the nuclear positions are C_{3v}, only C_s symmetry is imposed on the wavefunction; this relates to the inability for the MP2 calculation to handle degenerate representations. Hence the MO's are a' + a'' instead of a + e. The basis set is extended, TZVP + MP2, but excludes relativistic effects of course. The valence MO's show only small contributions to the EFG, except those three (sequence numbers 26, 27 and 31, e + a) which contain large populations of lone

pair character on iodine. However, all the valence MO's contribute much less to the EFG total electronic term than the 2p-5p MO's. The next comparison (Table 4) shows the valence shell contributions using both the smaller basis and the extended basis. Clearly the valence shell contribution, even from the lone-pair orbitals, is small relative to the core p-orbitals, a result to be expected owing to the latter being closer to the nuclei. The best experimental value is $\chi_{zz} = 1934.13022(39)$ MHz [37].

Although we don't consider further examples here, the Sn EFG requires similar treatment to I, while all of this section also applies to Br and Ge centres, but to a lesser extent. Hence, it is not surprising that by decontraction of the core AO's, there is a marked enhancement of EFG recovery even though the effect is small in each MO. One effect of this is to make it essential to operate with highly decontracted functions whenever electronic properties close to the nucleus are required. In the present paper we only consider results from these largest bases. With the increasing use of direct SCF and MP2 methods, especially on parallel processors, we are moving into the time when completely decontracted AO basis sets will become common.

Table 8. Mulliken Atomic Populations of Localised Orbitals.

| Compound | Type | s | p | d | s | p | d | n in sp^n |
|-------------------------|------------------|-------|-------|-------|-------|-------|-------|---------------|
| HCl | Cl_{LP} | 0.285 | 0.716 | 0.001 | | | | 2.515 |
| MeCl | Cl_{LP} | 0.286 | 0.713 | 0.000 | | | | 2.495 |
| HBr | Br_{LP} | 0.289 | 0.712 | 0.001 | | | | 2.463 |
| MeBr | Br_{LP} | 0.291 | 0.708 | 0.001 | | | | 2.433 |
| HI | I_{LP} | 0.296 | 0.708 | 0.001 | | | | 2.393 |
| MeI | I_{LP} | 0.301 | 0.705 | 0.001 | | | | 2.342 |
| MeCl | HC | 0.177 | 0.400 | 0.004 | 0.443 | 0.005 | | 2.260 |
| MeBr | HC | 0.178 | 0.395 | 0.004 | 0.443 | 0.005 | | 2.219 |
| MeI | HC | 0.171 | 0.414 | 0.004 | 0.433 | 0.005 | | 2.421 |
| HCl | HCl | 0.108 | 0.481 | 0.013 | 0.390 | 0.009 | | 4.454 |
| HBr | HBr | 0.100 | 0.464 | 0.016 | 0.413 | 0.008 | | 4.640 |
| HI | HI | 0.081 | 0.392 | 0.007 | 0.513 | 0.007 | | 4.840 |
| MeCl | CCl | 0.113 | 0.485 | 0.009 | 0.107 | 0.300 | 0.006 | 4.301 |
| MeBr | CBr | 0.099 | 0.319 | 0.005 | 0.108 | 0.476 | 0.010 | 3.222 |
| MeI | Cl | 0.162 | 0.393 | 0.004 | 0.081 | 0.382 | 0.004 | 2.426 |
| CF_3Cl | Cl_{LP} | 0.286 | 0.695 | 0.001 | | | | 3.433 |
| CF_3Cl | FLP | 0.272 | 0.701 | 0.000 | | | | 2.579 |
| CF_3Cl | CF | 0.103 | 0.212 | 0.014 | 0.127 | 0.548 | | 0.002 |
| CF_3Cl | CCl | 0.150 | 0.264 | 0.009 | 0.113 | 0.470 | 0.011 | 4.178 |
| SiH_3Cl | Cl_{LP} | 0.277 | 0.704 | 0.001 | | | | 2.538 |
| SiH_3Cl | SiH | 0.170 | 0.258 | 0.022 | 0.568 | 0.003 | | 1.518 |
| SiH_3Cl | SiCl | 0.089 | 0.179 | 0.024 | 0.137 | 0.577 | 0.006 | 4.222 |

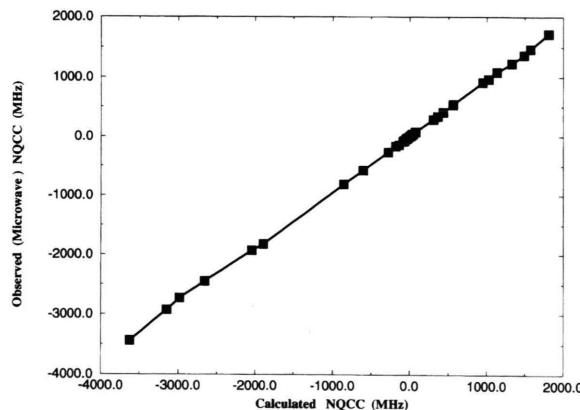


Fig. 1. Calc. NQCC (x) versus Obs. (y) in MHz. 60 Pt Regression: correlation coeff 0.9999; slope 0.9368; SE slope 0.0021.

4.3.2. Overall Correlation between Theory and Experiment

In Fig. 1 we give the overall correlation of ^{35}Cl , ^{79}Br , and ^{127}I data for axially symmetric molecules, basically C_{3v} and $C_{\infty v}$ structures. Only the ^{35}Cl and ^{79}Br isotopic data are shown in Table 6, and the experimental data are shown to the accuracy claimed by the original authors. The data establish a 60 point correlation line. The Calculated (x-axis) versus Observed NQCCs (y-axis) in Fig. 1 show a correlation coefficient of 0.9999, and the slope in 0.9368, with standard error in slope of 0.0021;

the intercept is 0.3000 with standard error of 2.3420, so the correlation line is statistically through the origin. These data were all obtained using the values for the atomic quadrupole moments (Q_Z) discussed above. Since the chloro, bromo and iodo compounds all lie on the same line, there seems no reason to question the relative values of the three halogen constants; this suggests that the problems over the scaling of the data in some previous studies arise from other factors. In short, there seems no reason to adopt a value 10% lower for $Q^{79}\text{Br}$ [18]; indeed, if this were done the bromo-compound data would differ from the correlation line shown by a significant amount. The germyl halides offer a further comparison with experimental data at both the halogen and Ge centre in some cases (above). The halogen NQCC's are in line with the other cases studied with smaller quadrivalent central atoms. The ^{73}Ge data in the fluoro- and chloro-germanes are very similar, in both the calculated EFG data and the MW experiments. Although there have been ^{119m}Sn halide data for the Sn centre for many years, [66, 11] most of the cases are highly substituted, and no real comparison with the present limited data is possible. Clearly the general level of agreement between experiment and the present level of theoretical study is very acceptable. Even the weakly bound halogen pentafluorides XF_5 ($\text{X} = \text{Cl}, \text{I}$) give acceptable values. Hence, overall, this enables us to use the experimental and theoretical data in a fairly interchangeable way when gross trends are being discussed.

Table 9. Localised Lone Pair Orbitals and Centroid Distance (a.u.) from Halogen.

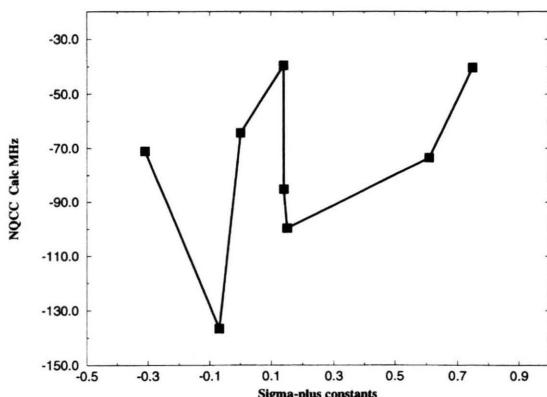
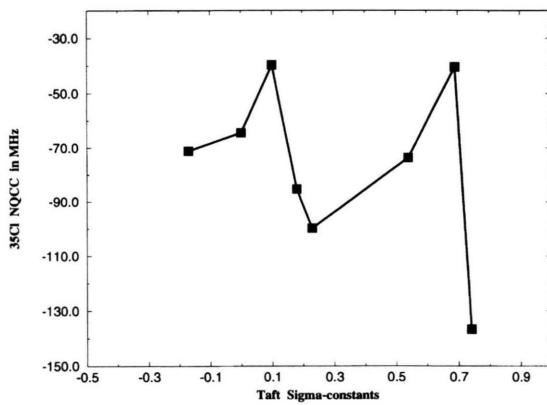
| Compound $\langle r \rangle$ | Compound $\langle r \rangle$ | Compound $\langle r \rangle$ | | | |
|------------------------------|------------------------------|------------------------------|-------|--------------------|-------|
| HCl | 0.834 | HBr | 0.940 | HI | 1.145 |
| MeCl | 0.843 | MeBr | 0.936 | MeI | 1.170 |
| CF ₃ Cl | 0.836 | CF ₃ Br | 0.949 | CF ₃ I | 1. |
| SiH ₃ Cl | 0.807 | SiH ₃ Br | 0.907 | SiH ₃ I | 1.114 |
| SiF ₃ Cl | 0.794 | SiF ₃ Br | 0.892 | SiF ₃ I | 1.095 |

Table 10. Localised Bond Orbitals at Halogen; Centroid Distance (a.u.) and EFG Contributions (a.u.).

| Compound | Bond | $\langle r \rangle$ | χ_{zz} |
|---------------------|------|---------------------|-------------|
| SiH ₃ Cl | SiCl | 1.318 | +3.143 |
| SiF ₃ Cl | SiCl | 1.333 | +3.080 |
| HCl | HCl | 1.484 | +2.811 |
| MeCl | CCl | 1.552 | +2.791 |
| CF ₃ Cl | CCl | 1.578 | +2.591 |
| SiH ₃ Br | SiBr | 1.531 | +5.391 |
| SiF ₃ Br | SiBr | 1.557 | +5.284 |
| HBr | HBr | 1.710 | +4.767 |
| MeBr | CBr | 1.773 | +4.650 |
| CF ₃ Br | CBr | 1.837 | +4.328 |
| SiH ₃ I | SiI | 1.892 | +6.422 |
| SiF ₃ I | SiI | 1.926 | +6.232 |
| HI | HI | 2.055 | +5.747 |
| MeI | CI | 2.127 | +5.570 |
| CF ₃ I | CI | | |

4.4. The Methyl and Silyl NQCC in Relation to Molecular Structure

As noted above, one type of substitution which leads to unexpected results is replacement of H₃ by F₃ in MX₃Cl (M = C, Si) and related compounds. The present results for this pair of compounds agree with experiment, that the fluoro-compound has a slightly higher (negative) NQCC at ³⁵Cl. The two silyl compounds are effectively identical, as observed experimentally. The Table of LMO populations clearly shows the comparison and reason for the similarities; thus for the chloromethane and chlorotrifluoromethane cases, the spⁿ hybridisation ratios (*n*) for the C-Cl bonds are 4.301 and 4.178, and the lone pair (LP) chlorine values for the spⁿ ratios on Cl are 2.433 and 2.495, respectively. Thus, within each of the pairs of LMO's, the hydrogen and fluoro compounds are similar. The same effect occurs in the silyl compounds. Comparison of methyl with silyl chlorides, however, leads to spⁿ ratios with *n* for the lone pair orbitals (C then Si) 2.495 and 2.538, while the C-Cl and Si-Cl bond contributions are 4.301 and 4.220, respectively; hence no difference is observed with these criteria. The reason does not lie with

Fig. 2. ³⁵Cl NQCC v. Taft sigma-plus constants. MeCl, FCl, HCl, H₃SiCl, ICl, BrCl, CF₃Cl, F₃SiCl.Fig. 3. ³⁵Cl NQCC Calc versus Taft sigma-constants. Compounds at peaks are SiH₃Cl and SiF₃Cl.

either the differences in the nuclear terms or with differences in polarisation of the core 2p_{Cl} orbitals. A comparison of the valence shell occupied MO's (1a₁ + 2e) shows that for each of the delocalised 1a₁ MO, the EFG z-axis contribution to the total EFG is +0.5 a.u. higher for the silyl- than the chloro-compounds; similarly, the 2e contributions differ by the remainder, leading to the observed 1 a.u. difference. There are associated small but distinct differences between the centroid positions of the LMO's on the halogens in the two series. Thus the LP_{Cl} are closer to Cl in the silyl than methyl compounds, implying more ionic character (born out by the Mulliken populations). Further, the group of centroid positions shown for the bond-LMO's in Table 10, show a clear correlation between the NQCC and the centroid position. As the bond-LMO centroid moves away from the Cl-atom, the NQCC shows a negative trend in magnitude.

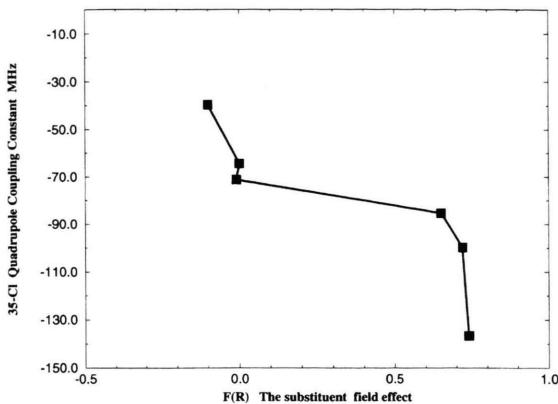


Fig. 4. ^{35}Cl QCC (MHz) versus $F(R)$ Field Constant. Swain and Lupton, *J. Amer. Chem. Soc.* **105**, 492, (1983).

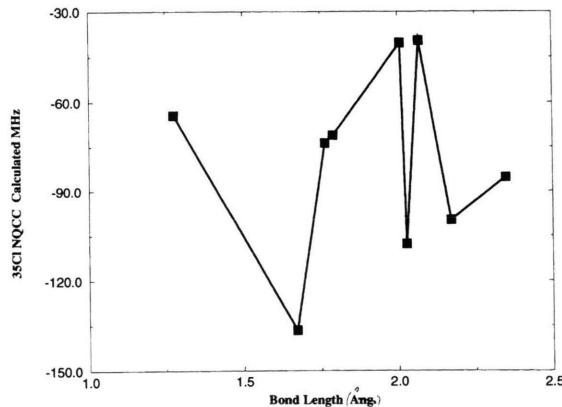


Fig. 5. ^{35}Cl NQCC versus Bond length. Sequence: HCl , FCl , CF_3Cl , CH_3Cl , SiF_3Cl , Cl_2 , SiH_3Cl , BrCl , ICl .

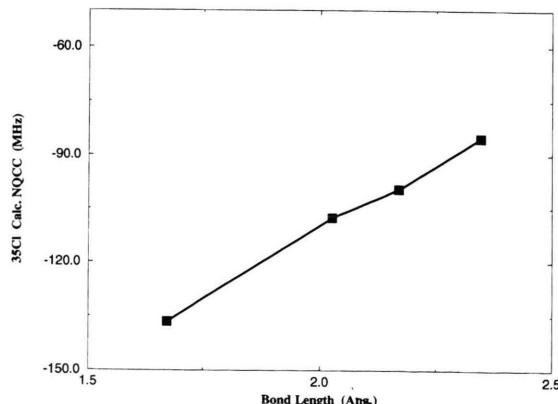


Fig. 6. Chloro-halogens: Bond Length v. ^{35}Cl NQCC. Compounds: FCl , Cl_2 , BrCl , ICl .

4.5. Overall Generalisations with Respect to Structure

If we plot the ^{35}Cl NQCC (in MHz) for a series of simple alkyl, silyl and other compounds against Taft σ - or σ^+ -constants, the data (Figs. 2 and 3) do not produce any correlation at all; similarly, the Swain and Lupton [67], [68, 69] set of substituent Field Effect data lead to a very poor correlation for the few compounds where the relevant $F(R)$ constants are available (Figure 4). If a set of simple molecules with widely differing bond lengths is plotted against ^{35}Cl NQCC, there is again no correlation (Fig. 5); such a procedure was successfully used to predict the ^{35}Cl NQCC for the chlorine molecule [70]. The principal difficulty with Fig. 6 that CX_3 and SiX_3 molecules ($X = \text{H}, \text{F}$) have almost the same NQCC, but significantly different bond lengths, and this is generally true for members of these series. Thus if we extract the series FCl , Cl_2 , BrCl , and ICl , then a clearly linear relation re-emerges (Figure 6). This is the basis for the evaluation of the ^{35}Cl NQCC for Cl_2 [70], where only diatomics are involved, in a set of specific linear correlations X-Cl , X-Br and X-I , NQCC versus bond length, and X is halogen.

4.6. Mulliken Atomic Populations at Equilibrium Structure

The net charges show wide variations, with some typical values for bonds in XY , in the sense $\text{X}^{\delta+}\text{-Y}^{\delta-}$ $\delta(\text{XY})$: 0.36 (HF), 0.20 (HCl), 0.17 (HBr), 0.08 (HI), 0.22 (ClF), 0.27 (BrF), 0.38 (IF), 0.02 (BrCl), 0.13 (ICl), and 0.12 (IBr). It is worth noting here that the atomic basis used for iodine, as supplemented above with the 'diffuse' terms is

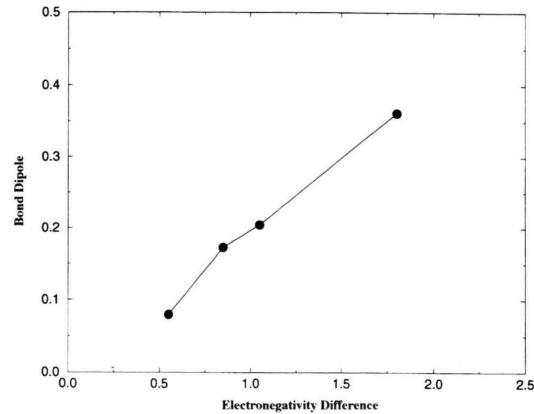


Fig. 7. Electronegativity Difference versus Bond Dipoles. Pauling scale.

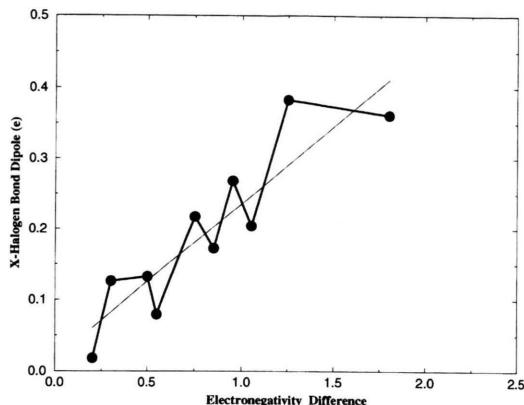


Fig. 8. Electronegativity Difference and Bond Dipoles. Pauling scale for Diatomics Only.

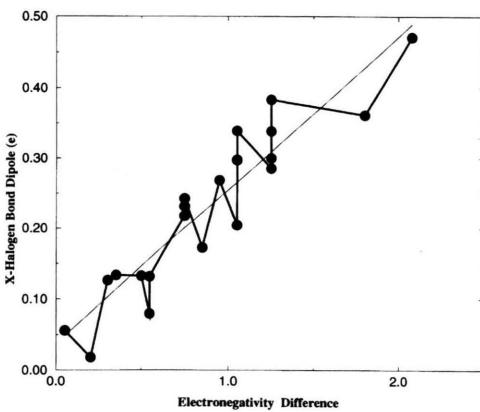


Fig. 9. Electronegativity Difference versus Bond Dipoles. Pauling scale: points HI, HCl, HBr, HF.

essential to generate this eminently reasonable set of bond dipoles; if the Huzinaga basis is used in its originally formulated manner, the I atom becomes much more electropositive, and indeed the dipole in HI changes direction to $H^{\delta+} - I^{\delta-}$. The reason is not lack of f-polarisation functions on I (or more generally for Sn as well), since when these are present the f-orbital populations are very small (and overall negative in nature). Various estimates of the electronegativity of the elements, such as the Mulliken scale, suggest that I(2.65) is more electronegative than H(2.1) (Fig. 7), and this of course leads to the normal dipole moment direction, as obtained with the 'diffuse' set here (Figure 8).

These bond dipoles, which are essentially local dipole moments relative to the free atoms, but as such do not contain any contribution from the lone pair electrons, can be obtained more generally in polyatomic molecules

[71], and are related to the bond 'ionicity' introduced in the interpretation of NQCC's for diatomic molecules [72]. In Fig. 9, we show the bond dipoles for the X-Halogen bonds for all the set of molecules studied here, namely the HX, XY, and H_3M-X set, where X, Y are halogens and M is C, Si, Ge, and Sn. Since the H_3 group must have some effect on the effective electronegativity of the attached M atom, the present data are very satisfactory; the linear regression correlation coefficient (22 sets of data) is 0.925, slope of correlation 0.217 (standard dev. 0.020), which is little changed by limitation to the diatomics only. Such a general correlation of ionic character in diatomics (XY) and electronegativity difference for X and Y has previously been established, but the data were based on Townes-Dailey analysis of the experimental NQCC, rather than entirely theoretical data [72].

5. Conclusions

The present study, with extended basis sets for both core and valence space, including MP2 correlation, leads to natural orbital wave-functions which give very good EFG-PA values in these compounds of axial symmetry. Since the equilibrium structures of the molecules described are very close to the spectroscopic ones, this means the centres of mass lie in similar positions relative to experiment.

We believe that the present results lie close to the s,p,d-limit for basis sets at the MP2 level. The present data strongly suggest that for singly bonded halogens, Cl, Br, and I, the contribution of f-orbital bonding is very small, and the absence of such functions from the EFG calculations is unimportant in the correlation with experiment. Even should this be shown to be incorrect, the strong correlation of data from Cl, Br, and I series would require the f-orbital contributions to be approximately equal and opposite to the relativistic contribution, which we are currently unable to calculate. Certainly the test cases where we have included f-orbitals at the equilibrium structure stage, show very small f-orbital contributions (less than 0.1e in total) at the MP2 level.

In the light of the single correlation line found for ^{35}Cl , ^{79}Br , and ^{127}I , we feel the ratios of the atomic quadrupole moments for these isotopes are correct. The only way this conclusion could be modified, would be for relativistic effects to scale the EFG-PA values in one direction with corresponding scaling of the atomic quadrupole moments in the other. This seems an improbable situation.

The ratios for CH_3X – 74.75 (X = ^{35}Cl), +577.14 (^{79}Br) and –1934.13 MHz (^{127}I) (i.e. 1:7.72 : 25.87) are fairly close to the cube of the atomic number ratios (1 : 8.73 : 30.30), and of course are a measure of $\langle 1/r^3 \rangle$. If the individual variation in the experimental isotopic quadrupole coupling constants is used to give the weighted ratios (χ_{zz}/Q_Z), then the ratios are 1.00 : 2.018 : 2.837, and are relatively close to 1 : 2 : 3 for ^{35}Cl , ^{79}Br , and ^{127}I , respectively.

Whilst the values for χ_{zz} in diverse compounds can be related to various types of physical-organic parameters, such as σ -constants in closely related groups of compounds, and similarly with other parameters such as σ^+ and the (Swain-Lupton) *F/R* parameters, these do not exist in widely differing types of compounds. Similarly, in the hydrogen halides and interhalogens, the correlations between the χ_{zz} and bond length are sufficiently satisfactory, to allow the estimation of the ^{35}Cl quadrupole coupling in the chlorine molecule with some confidence, but the correlation collapses when the bonding types are changed. For X-Y types of molecule, where X, Y are halogens, the bonding is basically as in ethane, with staggered lone-pairs; in organic molecules, the geometric arrangement of bonding pairs is similar, but the more extensive bonding range defeats the correlation. One reason is that the differing substituent effects of (say) H replacement by F in MX_3 -halogen, changes the effective electronegativity of M, but does not change the bonding distance M-halogen by the same amount.

In contrast, the LMO atomic compositions showing varying levels of sp^n hybrid orbital at each end of the A-B bond LMO, are helpful in giving more quantitative data. Thus the primary effect on the EFG-PA values is the nature of the atoms directly bonded, and hence the long-known correlation of NQCC with electronegativity differences, and especially to the detailed ratios of the sp^n character which this entails. The small differences arising

from σ -constants etc. then act as perturbations on top of these effects. The direct correlation of $\langle r \rangle$ with χ_{zz} shows that the electronegativity difference, by allowing movement of the bond LMO along the axis by differing amounts in a series of compounds, makes the halogen more or less atomic in character, as shown alternatively by the Mulliken populations. The electronegativity effect on the halogen lone pair positions evaluated by $\langle r \rangle$, is smaller but with similar effect. However, in the latter case, the spatial direction of the LP from the bond axis, makes the comparison more complex, owing to the large off-diagonal EFG elements for the LP-LMO's. In the comparison of alkyl and silyl halides, the differences cannot be ascribed to d-orbital participation in any meaningful way. The principal differences arise from the changes in the bond LMO composition.

Note Added in Proof:

Since this Paper was submitted, we have confirmed via a series of examples, that the effect of f-orbitals on iodine has a negligible effect upon the calculated EFG, and hence upon the calculated NQCC; to date these new results only refer to SCF rather than MP2 calculations, but we have shown that the SCF and MP2 results are very similar with these large bases. Typical examples are CH_3I and DF_3I , where the EFG data for the s,p,d (a), s,p,d,f(exponent 1.0) (b) and s,p,d,f(exponents 1.0, 4.0) (c) are as follows: CH_3I , (a) –10.2873, (b) –10.2030, (c) –10.1908; CF_3I , (a) –12.3566, (c) –12.2537 u.a.

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