The definition of a bond order in the iodine case, however, is not so unambiguous since both σ and π atomic orbitals are used to construct each molecular orbital. Advantage was taken of the mutual orthogonality of σ and π orbitals for Bond 1–2, and of $\tilde{\sigma}$ and $\tilde{\pi}$ orbitals (described in Sec. IIA) for Bond 2–3. For evaluating p_{12} the molecular orbitals were expressed in terms of atomic σ's and π's, and separate σ and π bond orders were evaluated from Eq. (31) by using, respectively, $c_{s\sigma 1}{}^{*}c_{s\sigma 2}$ and $c_{s\pi 1}{}^{*}c_{s\pi 2}$ terms. A corresponding procedure was used for p_{23}, except that the molecular orbitals were expressed in terms of $\tilde{\sigma}$'s and $\tilde{\pi}$'s. Values of the exchange integrals tabulated in Table IV were used, and the resulting bond orders are listed in Table VI. For comparison, the bond orders are tabulated for the isolated molecule approximation, corresponding to zero values of all intermolecular exchange integrals, β. The intermolecular interactions are seen to have only a small depressing effect on the total bond order of the 1–2 bond and to produce a bond order in the 2–3 bond almost one-third that in the 1–2 bond.

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Calculation of Chemical Shifts. I. General Formulation and the Z Dependence*

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Explicit expressions for the paramagnetic contribution $\sigma^{(2)}$ to the nuclear magnetic shielding are derived in the valence bond and the LCAO–MO framework including d as well as p orbitals on the atom in question. A survey of published experimental data reveals a periodic dependence of the range of chemical shifts on atomic number, which is explained in terms of the paramagnetic contribution to the chemical shift and its dependence on $\langle 1/r^3 \rangle$ for the bonding electrons.

A brief discussion is given of related but more complex periodicities in the electron coupling of nuclear spins, using the M–H coupling in Group IV hydrides as an example. It is suggested that the anisotropy in the nuclear shielding and internuclear coupling tensors may combine to give observable linewidth differences in the high-resolution NMR spectra of directly bonded nuclei of large Z.

I. INTRODUCTION

A GENERAL theory of chemical shifts was given by Ramsey.[1] Using second-order perturbation theory he expressed the nuclear magnetic shielding as the sum of two terms, a first-order term which is analogous to the Lamb formula for an isolated atom or ion, and a second-order term which is often called the paramagnetic term. The Lamb term is calculated easily, but in order to obtain accurate values of the second-order term one needs detailed knowledge of the energies and wavefunctions of all the electronic excited states. A simpler form is obtained by replacing the electronic excitation energies with an average value Δ. The quantum mechanical sum rule then leads to an expression involving only the ground state wavefunction. However even this form is difficult to use because for a large molecule both terms become large and mainly cancel each other.

Saika and Slichter[2] proposed a useful simplification. They divided the shielding tensor $\boldsymbol{\sigma}$ into separate *atomic* contributions: (1) $\boldsymbol{\sigma}^{(1)}$, the diamagnetic correction for the atom in question, (2) $\boldsymbol{\sigma}^{(2)}$, the paramagnetic term for the atom in question, and (3) $\boldsymbol{\sigma}^{(n)}$, the contribution from other atoms. By means of this approach, they found that changes in $\boldsymbol{\sigma}^{(2)}$ accounted for the main general aspects of fluorine chemical shifts, the range of 63×10^{-6} and the dependence upon the M–F bond

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ionic character. With the origin thus centered on the nucleus in question, the $\sigma^{(2)}$ contribution lends itself to calculation in terms of conventional, localized bond properties such as hybridization and ionic and double-bond character. Therefore, it is of interest to review the circumstances when $\sigma^{(2)}$ may dominate the chemical shift of a nucleus.

The fractional differences in the diamagnetic term $\sigma^{(1)}$ caused by changes in bond properties are small compared to the changes in $\sigma^{(2)}$ *for atoms other than hydrogen.* Calculations of $\sigma^{(1)}$ for neutral atoms from Hartree–Fock wavefunctions have been performed by Dickerson[3] for $Z=1$ to 92. In his results, $\sigma_{\text{atom}}^{(1)}$ increases monotonically with Z, ranging from 1.8×10^{-5} in H, 46.4×10^{-5} in F, 559×10^{-5} in Xe up to 1160×10^{-5} in U. However, in molecule formation it is mainly the outer electrons which are disturbed, and Dickerson's calculations show that the percentage contribution of the *outer* electrons to $\sigma^{(1)}$ decreases markedly with Z. Thus, chemical changes in $\sigma^{(1)}$ for H are of the same magnitude as the total proton shielding, while for Xe, for example, only about 0.075% of $\sigma^{(1)}$ comes from each $5p$ electron and the $\sigma^{(1)}$ contribution to Xe chemical shifts is correspondingly small, at most 4 ppm per $5p$ electron.

All other contributions to σ are lumped together in $\sigma^{(n)}$, including "neighbor anisotropy" contributions and the effects of ring currents and intermolecular interactions. Of these contributions, the nuclear shielding by electron circulations on neighboring atoms falls off as the inverse cube of the distance of the neighbor from the atom in question and have been estimated by Pople[4,5] as unlikely to exceed 10^{-5} in magnitude. Of similar maximum magnitude are the effects of intermolecular interactions[6,7] and of ring currents.[7]

TABLE I. "Multiplication table" for angular momentum operators and p atomic functions.[a]

Operator	p_x	p_y	p_z
l_x	0	$-p_z$	p_y
l_y	p_z	0	$-p_x$
l_z	$-p_y$	p_x	0
l_xl_x	0	$-p_y$	$-p_z$
l_yl_y	$-p_x$	0	$-p_z$
l_zl_z	$-p_x$	$-p_y$	0

[a] The entries in the first three rows are in units of $(\hbar/i)$; those in the last three rows are in units of $(-\hbar^2)$.

TABLE II. Matrix elements of the angular momentum operators.[a]

	p_x			p_y			p_z		
p_x	0	0	0	0	0	1	0	−1	0
	0	−1	−1	0	0	0	0	0	0
p_y	0	0	−1	0	0	0	1	0	0
	0	0	0	−1	0	−1	0	0	0
p_z	0	1	0	−1	0	0	0	0	0
	0	0	0	0	0	0	−1	−1	0

[a] The format used in presenting the matrix elements is defined in Table V.

In contrast to the approximate ranges of 10^{-5} for chemical changes in $\sigma^{(1)}$ and $\sigma^{(n)}$, it has been noted[8] that the range of chemical shifts for a nucleus is of the same order of magnitude as the total shielding for the free atom. For example, proton chemical shifts[7] cover a range of about 2×10^{-5} and Tl,[9] about 480×10^{-5}. Therefore, it is evident that $\sigma^{(2)}$ must be by far the dominant term for all but the lightest nuclei except in unusual circumstances. This view is supported not only by the original work of Saika and Slichter[2] on F but also by more recent calculations for F,[10] P,[11,12] Hg,[9] Pb,[9,13] and Tl,[9] in which various approximations have been used to express $\sigma^{(2)}$ in terms of localized bond properties. These calculations of $\sigma^{(2)}$ are limited to the valence electrons of the atom. The core electrons are assumed to remain the same in going from one molecule to another, and being spherically symmetric by this assumption, the core contributes nothing to the paramagnetic term. This approximation appears to be reasonable, at least it is a convenience which we also adopt. Nonetheless, a check on the effects of core polarization on $\sigma^{(2)}$ is desirable.

A convenient form was introduced for $\sigma^{(2)}$ by Pople[5] and Karplus and Das[10] who expressed it in terms of orbital populations $p_{\mu\nu}$ in an LCAO–MO framework. However, they treated only p orbitals centered on the atom in question. In the present work explicit expressions for $\sigma^{(2)}$ are derived in the valence bond and the LCAO–MO framework, including d as well as p orbitals on the atom in question.

A review of the chemical shift ranges observed for twenty elements reveals two periodic trends. The range of chemical shifts increases with atomic number Z for elements of the same group in the periodic table and

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TABLE III. "Multiplication table" for angular momentum operators and d atomic functions.[a]

Operators	d_{z^2}	d_{yz}	d_{xz}	d_{xy}	$d_{x^2+y^2}$
ℓ_x	$\sqrt{3}d_{xz}$	d_{xy}	$-(\sqrt{3}d_{z^2}+d_{x^2+y^2})$	$-d_{yz}$	d_{xz}
ℓ_y	$-\sqrt{3}d_{yz}$	$(\sqrt{3}d_{z^2}-d_{x^2+y^2})$	$-d_{xy}$	d_{xz}	d_{yz}
ℓ_z	0	$-d_{xz}$	d_{yz}	$2d_{x^2+y^2}$	$-2d_{xy}$
$\ell_x\ell_x$	$-(3d_{z^2}+\sqrt{3}d_{x^2+y^2})$	$-d_{yz}$	$-4d_{xz}$	$-d_{xy}$	$-(\sqrt{3}d_{z^2}+d_{x^2+y^2})$
$\ell_y\ell_y$	$-(3d_{z^2}-\sqrt{3}d_{x^2+y^2})$	$-4d_{yz}$	$-d_{xz}$	$-d_{xy}$	$(\sqrt{3}d_{z^2}-d_{x^2+y^2})$
$\ell_z\ell_z$	0	$-d_{yz}$	$-d_{xz}$	$-4d_{xy}$	$-4d_{x^2+y^2}$

[a] The entries in the first three rows are in units of $(\hbar/i)$; those in the last three rows are in units of $(-\hbar^2)$.

also it increases with Z along a period. These trends agree with the magnitude calculated for the paramagnetic contribution to the chemical shift and its dependence on $\langle 1/r^3\rangle$ for the bonding electrons. The atomic spin-orbit interactions are used to estimate the Z dependence of $\langle 1/r^3\rangle$.

II. GENERAL FORMULATION FOR $\sigma^{(2)}$ IN THE LCAO–MO AND VALENCE BOND FRAMEWORK

The calculation of $\sigma^{(2)}$ requires evaluation of matrix elements of the form

$$\langle\phi_i \mid \ell_x/r^3 \mid \phi_j\rangle \quad \text{and} \quad \langle\phi_i \mid \ell_x\ell_x/r^3 \mid \phi_j\rangle,$$

where ℓ_x operates only on the θ and ϕ parts of the atomic orbital ϕ_j. Here we will use the notation of Pauling for the d orbitals whose θ and ϕ dependence are shown below:

$$d_{z^2}=(5/4)^{\frac{1}{2}}(3\cos^2\theta-1),$$
$$d_{yz}=(15)^{\frac{1}{2}}\sin\theta\cos\theta\cos\phi,$$
$$d_{xz}=(15)^{\frac{1}{2}}\sin\theta\cos\theta\sin\phi,$$
$$d_{x^2+y^2}=(15/4)^{\frac{1}{2}}\sin^2\theta\cos 2\phi,$$
$$d_{xy}=(15/4)^{\frac{1}{2}}\sin^2\theta\sin 2\phi.$$

Using the usual operator forms of ℓ_x, ℓ_y, and ℓ_z, namely

$$\ell_x=\left(-\frac{\hbar}{i}\right)\left(\sin\phi\frac{\partial}{\partial\theta}+\cot\theta\cos\phi\frac{\partial}{\partial\phi}\right),$$

$$\ell_y=\left(\frac{\hbar}{i}\right)\left(\cos\phi\frac{\partial}{\partial\theta}-\cot\theta\sin\phi\frac{\partial}{\partial\phi}\right),$$

and

$$\ell_z=\left(\frac{\hbar}{i}\right)\frac{\partial}{\partial\phi},$$

we obtain the "multiplication tables" for the angular momentum operators and the table of matrix elements given in Tables I and II for p atomic functions and in Tables III and IV for the d. The matrix elements in Tables II and IV occur in groups of six; the format used in presenting them is defined in Table V.

Having all the matrix elements needed, we may now express $\sigma^{(2)}$ in the LCAO–MO and in the valence bond framework, in terms primarily the atomic orbitals on the atom for which $\sigma^{(2)}$ is being calculated.

TABLE IV. Matrix elements of the angular momentum operators.[a]

	d_{z^2}			d_{yz}			d_{xz}			d_{xy}			$d_{x^2+y^2}$		
d_{z^2}	0	0	0	0	$\sqrt{3}$	0	$-\sqrt{3}$	0	0	0	0	0	0	0	0
	-3	-3	0	0	0	0	0	0	0	0	0	0	$-\sqrt{3}$	$\sqrt{3}$	0
d_{yz}	0	$-\sqrt{3}$	0	0	0	0	0	0	1	-1	0	0	0	1	0
	0	0	0	-1	-4	-1	0	0	0	0	0	0	0	0	0
d_{xz}	$\sqrt{3}$	0	0	0	0	-1	0	0	0	0	1	0	1	0	0
	0	0	0	0	0	0	-4	-1	-1	0	0	0	0	0	0
d_{xy}	0	0	0	1	0	0	0	-1	0	0	0	0	0	0	-2
	0	0	0	0	0	0	0	0	0	-1	-1	-4	0	0	0
$d_{x^2+y^2}$	0	0	0	0	-1	0	-1	0	0	0	0	2	0	0	0
	$-\sqrt{3}$	$\sqrt{3}$	0	0	0	0	0	0	0	0	0	0	-1	-1	-4

[a] The format used in presenting the matrix elements is defined in Table V.

LCAO-MO Formulation for $\sigma^{(2)}$

A typical molecular orbital formed by a linear combination of s, p, and d atomic orbitals on the atom in question, and other orbitals on the other atoms, may be written as follows:

$$\psi_a = a_x p_x + a_y p_y + a_z p_z + a_{z^2} d_{z^2} + a_{xy} d_{xy} + a_{xz} d_{xz} + a_{yz} d_{yz} + a_{x^2+y^2} d_{x^2+y^2} + s \text{ orbitals} + \text{orbitals on other atoms}. \quad (1)$$

Let the orbital population $p_{\mu\nu}$ be defined as

$$p_{\mu\nu} = \sum_a n_a (a_\mu a_\nu^*), \quad (2)$$

where n_a is the number of electrons in the ath molecular orbital, usually two, a_μ and a_ν are the coefficients of the atomic orbitals μ and ν in ψ_a, and the summation extends over all molecular orbitals a. The quantity $p_{\mu\nu}$ is generally called a matrix element of the charge and bond order matrix. The expression for $\sigma^{(2)}$ in terms of $p_{\mu\nu}$ and the average excitation energy Δ is given below.[10]

$$\sigma^{(2)} = (e^2/\Delta m^2 c^2) \sum_{\mu,\nu} p_{\mu\nu} \{ \langle \phi_\nu(k) \mid \mathfrak{l}_k \mathfrak{l}_k / r_k^3 \mid \phi_\mu(k) \rangle - \sum_{\lambda,\rho} (\tfrac{1}{2}) p_{\rho\lambda} \langle \phi_\nu(k) \mid \mathfrak{l}_k / r_k^3 \mid \phi_\rho(k) \rangle \langle \phi_\lambda(k) \mid \mathfrak{l}_k \mid \phi_\mu(k) \rangle \}. \quad (3)$$

TABLE V. Definition of format used for matrix elements in Tables II and IV.

	A		
B	$\langle B \mid i\mathfrak{l}_x/\hbar \mid A \rangle$	$\langle B \mid i\mathfrak{l}_y/\hbar \mid A \rangle$	$\langle B \mid i\mathfrak{l}_z/\hbar \mid A \rangle$
	$\langle B \mid -\mathfrak{l}_x\mathfrak{l}_z/\hbar^2 \mid A \rangle$	$\langle B \mid -\mathfrak{l}_y\mathfrak{l}_y/\hbar^2 \mid A \rangle$	$\langle B \mid -\mathfrak{l}_z\mathfrak{l}_z/\hbar^2 \mid A \rangle$

The average of $\sigma^{(2)}$ over all orientations, which is of course the contribution to the nuclear shielding observed in liquids and gases, is given by $\frac{1}{3}$ the trace of $\sigma^{(2)}$,

$$\sigma^{(2)} \equiv \sigma_{Av}^{(2)} = \tfrac{1}{3}(\sigma_{xx}^{(2)} + \sigma_{yy}^{(2)} + \sigma_{zz}^{(2)}), \quad (4)$$

where the expression for $\sigma_{\alpha\alpha}^{(2)}$ ($\alpha = x, y, z$) is as in Eq. (3) except that $\mathfrak{l}_k$ is replaced by its α component $\ell_{k\alpha}$. The matrix elements needed to evaluate Eq. (4) are given in Tables II and IV presented in the introduction to this section. The r_k^{-3} operators are averaged over the radial part of the atomic wavefunction and for simplicity we denote by $\langle 1/r^3 \rangle_p$ the average value of r^{-3} over the p_x, p_y, and p_z orbitals, similarly for $\langle 1/r^3 \rangle_d$. The resulting expressions for $\sigma_{zz}^{(2)}$, $\sigma_{xx}^{(2)}$, and $\sigma_{yy}^{(2)}$ in terms of $p_{\mu\nu}$ are given in Appendix A and the rotational average of $\sigma^{(2)}$ is given below:

$$\begin{aligned}
\sigma_{Av}^{(2)} = -(2e^2\hbar^2/3\Delta m^2 c^2) \{ & \langle 1/r^3 \rangle_p [(p_{xx}+p_{yy}+p_{zz}) - \tfrac{1}{2}(p_{zz}p_{yy}+p_{xx}p_{yy}+p_{xx}p_{zz}) + \tfrac{1}{2}(p_{yz}p_{zy}+p_{xy}p_{yx}+p_{xz}p_{zx})] \\
& + \langle 1/r^3 \rangle_d \{ 3(p_{z^2,z^2}+p_{xz,xz}+p_{xy,xy}+p_{x^2+y^2,x^2+y^2}+p_{yz,yz}) - \tfrac{3}{2}(\tfrac{4}{3}p_{x^2+y^2,x^2+y^2}p_{xy,xy}+p_{z^2,z^2}p_{xz,xz}+p_{z^2,z^2}p_{yz,yz}) \\
& - \tfrac{1}{2}(p_{x^2+y^2,x^2+y^2}p_{xz,xz}+p_{x^2+y^2,x^2+y^2}p_{yz,yz}+p_{xy,xy}p_{yz,yz}+p_{xy,xy}p_{xz,xz}+p_{xz,xz}p_{yz,yz}) \\
& + \tfrac{3}{2}(\tfrac{4}{3}p_{x^2+y^2,xy}p_{xy,x^2+y^2}+p_{z^2,xz}p_{xz,z^2}+p_{z^2,yz}p_{yz,z^2}) \\
& + \tfrac{1}{2}(p_{x^2+y^2,xz}p_{xz,x^2+y^2}+p_{x^2+y^2,yz}p_{yz,x^2+y^2}+p_{xy,yz}p_{yz,xy}+p_{xy,xz}p_{xz,xy}+p_{xz,yz}p_{yz,xz}) \\
& + (\sqrt{3}/2)[(p_{yz,yz}-p_{xz,xz})(p_{x^2+y^2,z^2}+p_{z^2,x^2+y^2}) + (p_{xy,z^2}+p_{z^2,xy})(p_{yz,xz}+p_{xz,yz}) \\
& - (p_{z^2,yz}p_{xz,xy}+p_{yz,z^2}p_{xy,xz}+p_{z^2,xz}p_{yz,xy}+p_{xz,z^2}p_{xy,yz}) \\
& + p_{z^2,yz}p_{yz,x^2+y^2}+p_{x^2+y^2,yz}p_{yz,z^2}+p_{x^2+y^2,xz}p_{xz,z^2}+p_{z^2,xz}p_{xz,x^2+y^2}] \\
& + \tfrac{1}{2}[p_{x^2+y^2,xz}(2p_{xy,yz}+p_{yz,xy}) + p_{xz,x^2+y^2}(p_{xy,yz}+2p_{yz,xy}) \\
& - p_{x^2+y^2,yz}(2p_{xy,xz}+p_{xz,xy}) - p_{yz,x^2+y^2}(p_{xy,xz}+2p_{xz,xy}) + (p_{yz,xz}-p_{xz,yz})(p_{xy,x^2+y^2}-p_{x^2+y^2,xy})]\}). \quad (5)
\end{aligned}$$

The first part of Eq. (5), for the p orbitals, is identical to that given by Karplus and Das[10]; the rest of the expression involving d orbitals is given here for the first time. As a check, the orbital populations for an atom with closed p and d shells, $p_{ii}=2$, $p_{ij}=0$, were substituted and $\sigma^{(2)}$ went to zero as expected.

Valence Bond Formulation for $\sigma^{(2)}$

For a $2n$ electron case, the perfect pairing wavefunction may be written as a separated pair wavefunction

$$\Psi = [2^n/(2n)!]^{\frac{1}{2}} \times \sum_P (-1)^P P\{\psi_{ax}(1,2)\psi_{by}(3,4)\psi_{cz}(5,6)\cdots\}, \quad (6)$$

where P permutes electrons between pairs. The functions for the separated pairs are

$$\psi_{ax}(i,j) = u_{ax}(i,j)[\alpha(i)\beta(j) - \beta(i)\alpha(j)]/\sqrt{2}, \quad (7)$$

in which

$$u_{ax}(1,2)=\eta_{ax}[\phi_a(1)\phi_x(2)+\phi_x(1)\phi_a(2)+\lambda_a\phi_a(1)\phi_a(2)+\lambda_x\phi_x(1)\phi_x(2)], \quad (8)$$

where η is the normalization constant and the λ's are coefficients describing the ionic character of the bond. We let ϕ_a, ϕ_b, $\cdots$ stand for atomic orbitals on the atom in question and ϕ_x, ϕ_y, $\cdots$ for atomic orbitals on the atoms bonded to it.

The expression for $\mathfrak{d}^{(2)}$ is then given by

$$\mathfrak{d}^{(2)}=-\frac{e^2}{\Delta m^2c^2}\frac{2^n}{(2n)!}\times[\sum_P(-1)^PP\{\ \}\mid\sum_{k,k'}\mathfrak{l}_k\mathfrak{l}_{k'}/r_k^3\mid\sum_P(-1)^PP\{\ \}]. \quad (9)$$

In Eq. (9), the first permutation sum has $(2n)!/2^n$ terms which yield identical matrix elements and hence cancels out the coefficient $2^n/(2n)!$. This leaves

$$\mathfrak{d}^{(2)}=-\frac{e^2}{\Delta m^2c^2}\times[\psi_{ax}(1,2)\psi_{by}(3,4)\cdots\mid\sum_{k,k'}\mathfrak{l}_k\mathfrak{l}_{k'}/r_k^3\mid\sum_P(-1)^PP\{\ \}]. \quad (10)$$

The unpermuted term of Eq. (10) gives rise to I+II+III:

$$\mathrm{I}=2\sum_{r=1}^{n}\langle u_r(i,j)\mid\mathfrak{l}_i\mathfrak{l}_i/r_i^3\mid u_r(i,j)\rangle, \quad (11)$$

$$\mathrm{II}=2\sum_{r=1}^{n}\langle u_r(i,j)\mid\mathfrak{l}_i\mathfrak{l}_j/r_i^3\mid u_r(i,j)\rangle, \quad (12)$$

$$\mathrm{III}=8\sum_{r}^{}\sum_{s>r}^{}\langle u_r(i,j)\mid\mathfrak{l}_i/r_i^3\mid u_r(i,j)\rangle\times\langle u_s(k,l)\mid\mathfrak{l}_k\mid u_s(k,l)\rangle, \quad (13)$$

where III has $n(n-1)/2$ terms. In Eq. (10) the permuted terms involving more than one permutation give vanishing matrix elements as long as the geminals $\psi_r(i,j)$ obey the one-electron orthogonality rule

$$\int\psi_r(i,j)\psi_s(i,k)\,d\tau_i=0.$$

For a single permutation of electrons which are not antisymmetrized, a factor of $+\frac{1}{2}$ arises in the integration over the spin coordinates, and also a factor of -1 because of the odd parity of a single permutation. Hence the singly permutated term of Eq. (10) gives rise to IV:

$$\mathrm{IV}=-(1/2)8\sum_{r}^{}\sum_{s>r}^{}\times\langle u_r(k,j)u_s(i,l)\mid\mathfrak{l}_k\mathfrak{l}_i/r_k^3\mid u_s(k,l)u_r(i,j)\rangle. \quad (14)$$

If we drop all matrix elements involving ϕ_x, $\phi_y\cdots$ (i.e., all orbitals centered on atoms other than the one of interest), as is usually done, then

$$\mathrm{I}+\mathrm{II}=2\sum_{r=1}^{n}\eta_{ax}^2\{(1+\lambda_a^2)\langle\phi_a(1)\mid\mathfrak{l}_1\mathfrak{l}_1/r_1^3\mid\phi_a(1)\rangle+\lambda_a^2\langle\phi_a(1)\mid\mathfrak{l}_1/r_1^3\mid\phi_a(1)\rangle\langle\phi_a(1)\mid\mathfrak{l}_1\mid\phi_a(1)\rangle\}, \quad (15)$$

$$\mathrm{III}=8\sum_{r}^{}\sum_{s>r}^{}\eta_{ax}^2\eta_{by}^2(1+\lambda_a^2)(1+\lambda_b^2)\times\langle\phi_a(1)\mid\mathfrak{l}_1/r_1^3\mid\phi_a(1)\rangle\langle\phi_b(1)\mid\mathfrak{l}_1\mid\phi_b(1)\rangle, \quad (16)$$

$$\mathrm{IV}=-4\sum_{r}^{}\sum_{s>r}^{}\eta_{ax}^2\eta_{by}^2(1+\lambda_a^2)(1+\lambda_b^2)\times\langle\phi_a(1)\mid\mathfrak{l}_1/r_1^3\mid\phi_b(1)\rangle\langle\phi_b(1)\mid\mathfrak{l}_1\mid\phi_a(1)\rangle. \quad (17)$$

We find that all $\langle\phi_a(1)\mid\ell_{x1}\mid\phi_a(1)\rangle=0$ and similarly for the other two components of $\mathfrak{l}$. Thereby, the final expression for $\sigma^{(2)}$ is greatly simplified. For $\sigma_{xx}^{(2)}$ we obtain

$$\sigma_{xx}^{(2)}=-(2e^2/\Delta m^2c^2)\{\sum_{r=1}^{n}\eta_{ax}^2(1+\lambda_a^2)\langle\phi_a\mid\ell_x\ell_x/r^3\mid\phi_a\rangle-2\sum_{r>s}\sum\eta_{ax}^2\eta_{by}^2(1+\lambda_a^2)(1+\lambda_b^2)\times\langle\phi_a\mid\ell_x/r^3\mid\phi_b\rangle\langle\phi_b\mid\ell_x\mid\phi_a\rangle\}, \quad (18)$$

with completely analogous expressions for $\sigma_{yy}^{(2)}$ and $\sigma_{zz}^{(2)}$. As before $\sigma^{(2)}$ is given by Eq. (4), and the final result is in a form which can easily be applied to a perfect pairing wavefunction.

If only s, p and d orbitals are involved, i.e., when

$$\phi_a=c_s^as+c_x^ap_x+c_y^ap_y+c_z^ap_z+c_{z^2}^ad_{z^2}+\cdots+c_{xy}^ad_{xy}, \quad (19)$$

the equation for $\sigma^{(2)}$ can now be written in a more explicit form by using the results in Tables II and IV. Thus, we obtain the expressions for $\sigma_{xx}^{(2)}$, $\sigma_{yy}^{(2)}$, and $\sigma_{zz}^{(2)}$ given in Appendix B. The resultant average of $\mathfrak{d}^{(2)}$ over all orientations is:

$$\sigma^{(2)}=-\tfrac{4}{5}(e^2\hbar^2/\Delta m^2c^2)\{\langle1/r^3\rangle_p[\sum_{r=1}^{n}\eta_{ax}^2(1+\lambda_a^2)P^a-\sum_{r>s}\sum\eta_{ax}^2\eta_{by}^2(1+\lambda_a^2)(1+\lambda_b^2)P^{ab}]+\langle1/r^3\rangle_d[3\sum_{r=1}^{n}\eta_{ax}^2(1+\lambda_a^2)D^a-\sum_{r>s}\sum\eta_{ax}^2\eta_{by}^2(1+\lambda_a^2)(1+\lambda_b^2)D^{ab}]\}, \quad (20)$$

where

$$P^a=\sum_{i=x,y,z}(c_i^a)^2,\qquad D^a=\sum_{i=z^2,xz,\ldots}(c_i^a)^2,$$

$$P^{ab}=(c_z^ac_y^b-c_y^ac_z^b)^2+(c_x^ac_z^b-c_z^ac_x^b)^2+(c_x^ac_y^b-c_y^ac_x^b)^2,$$

and

$$D^{ab}=[\sqrt{3}(c_{xz}{}^{a}c_{z^2}{}^{b}-c_{z^2}{}^{a}c_{xz}{}^{b})+(c_{xy}{}^{a}c_{yz}{}^{b}-c_{yz}{}^{a}c_{xy}{}^{b})+(c_{xz}{}^{a}c_{x^2+y^2}{}^{b}-c_{x^2+y^2}{}^{a}c_{xz}{}^{b})]^2$$
$$+[\sqrt{3}(c_{z^2}{}^{a}c_{yz}{}^{b}-c_{yz}{}^{a}c_{z^2}{}^{b})+(c_{yz}{}^{a}c_{x^2+y^2}{}^{b}-c_{x^2+y^2}{}^{a}c_{yz}{}^{b})+(c_{xz}{}^{a}c_{xy}{}^{b}-c_{xy}{}^{a}c_{xz}{}^{b})]^2$$
$$+[2(c_{x^2+y^2}{}^{a}c_{xy}{}^{b}-c_{xy}{}^{a}c_{x^2+y^2}{}^{b})+(c_{yz}{}^{a}c_{xz}{}^{b}-c_{xz}{}^{a}c_{yz}{}^{b})]^2.$$

In this approximation, we have $\eta_{ax}{}^2=(2+\lambda_a{}^2+\lambda_x{}^2)^{-1}$. For the case where $\psi_{ax}(1,2)$ is $\psi_{aa}(1,2)$, i.e., a lone pair in the ϕ_a orbital, we use $\eta_{aa}{}^2(1+\lambda_a{}^2)=1$.

Comments on MO and VB Formulations

The quantity in the valence bond formulation which corresponds to orbital population is

$$p_{\mu\mu}=2\sum_{\text{bonds }ax}\eta_{ax}{}^2(1+\lambda_a{}^2)(c_\mu{}^a)^2. \quad (21)$$

With this in mind, examination of the VB and MO expressions for $\sigma_{\alpha\alpha}{}^{(2)}(\alpha=x,y,z)$ given in Appendices A and B reveals their close similarity. This is not unexpected.

In both formulations, the bonding orbitals centered on atoms other than that for which $\sigma^{(2)}$ is calculated exert implicit effects upon $\sigma^{(2)}$ by affecting Δ and localized bond properties such as ionicity and bond order. A more direct effect is their influence upon $p_{\mu\nu}$ and $p_{\mu\mu}$ in Eqs. (2) and (21) via normalization of the bonding functions in Eqs. (1) and (8). However, the normalization may require overlap integrals which are not readily available. For this or other reasons the calculation of $\sigma^{(2)}$ can be simplified considerably by dropping from Eqs. (2) and (21) any terms directly involving the atomic orbitals centered elsewhere than on the nucleus for which $\sigma^{(2)}$ is being calculated. The importance of this approximation depends of course upon the particular system in question. But it appears to be a reasonable procedure at least in dealing with an homologous series of compounds such as the fluorobenzenes.[10]

IV. Z DEPENDENCE OF CHEMICAL SHIFTS

It has been noted that, in general, the range of chemical shifts in different compounds (by this we mean the difference between the chemical shifts of the lowest field and highest field signals for a particular nuclear species) increases with increasing atomic number, Z.[8,9] Furthermore, a survey of the now-extensive experimental data available reveals that this trend is periodic, as shown by the summary given in Table VI. The range of chemical shifts increases with atomic number Z for a particular group, and also increases with Z along a period. The only apparent exceptions are N, O, and F, for which the general trends may be reversed by an increase in the shift range with the number of bonding orbitals employed, and Si for which the small range is most probably due to limited information.

Relation between $\sigma^{(2)}$ and $\langle 1/r^3\rangle$

Inspection of Eqs. (5) and (20) shows that the paramagnetic term is essentially of the form

$$\sigma^{(2)}=-(2e^2\hbar^2/3\Delta m^2c^2)(\langle 1/r^3\rangle_p P_u+\langle 1/r^3\rangle_d D_u) \quad (21)$$

where P_u and D_u represent the "unbalance" of the valence electrons in the p and d orbitals centered on the atom in question. For example, for p electrons in the LCAO–MO formulation, P_u is defined by Eq. (5) in terms of the orbital populations as

$$P_u=p_{xx}+p_{yy}+p_{zz}-\tfrac{1}{2}(p_{xx}p_{zz}+p_{yy}p_{xx}+p_{yy}p_{zz})$$
$$+\tfrac{1}{2}(p_{xy}p_{yx}+p_{xz}p_{zx}+p_{zy}p_{yz}). \quad (22)$$

The parameters Δ, $\langle 1/r^3\rangle_p$, and $\langle 1/r^3\rangle_d$, and P_u and D_u determine the magnitude of $\sigma^{(2)}$ and of the changes in it. Of these, the average excitation energy Δ exhibits about as much variation for different chemical states of an element as for compounds of different elements. Also, Δ covers a relatively small, two- or threefold range. Therefore, the major periodicities of the chemical shift range are not due to Δ.

The numerical values of P_u and D_u depend largely upon the coordination number of the atom, the hybridization of its bonding orbitals and the ionicity of its bonds. In the spherically symmetric closed shell case, P_u and D_u both have their minimum value of zero, which corresponds to a free, diamagnetic ion or an inert gas. On the other hand, the maximum values of P_u and D_u correspond to the maximum "unbalance" of electron distribution. The maximum for P_u is 2, which occurs for example when two p orbitals are filled ($p_{\mu\mu}=2$) and one is empty ($p_{\nu\nu}=0$), or one filled and two empty. The expression for D_u is more difficult to analyze, but it appears that the maximum value is 12, which occurs, for example when the three t_{2g} d orbitals are filled and the two e_g are empty or when the two are filled and the three empty.

For any particular atom in different chemical states, the ranges in P_u and D_u are governed by these limits of 0 to 2 and 0 to 12, respectively. Within a given atomic period, the elements have different numbers and/or types of bonding orbitals, so the ranges found in P_u and in D_u would be somewhat different. For example, the maximum P_u for fluorine is 1 (one p orbital with $p_{\mu\mu}=1$) while for carbon it is $\frac{3}{2}$ (three p orbitals with $p_{\mu\mu}=1$).

This could account for the apparent nonperiodicity of the N, O, and F chemical shift ranges, which was

TABLE VI. Range of chemical shifts (ppm).

n	ns	ns^2	np	np^2	np^3	np^4	np^5	np^6
1	H[a] 20							
2	Li[b] 5		B[c] 140	C[d] 316	N[e] 626	O[f] 690	F[a,g] 625	
3			Al[h] 220	Si[i] 140	P[j] 670		Cl[k] 820	
4						Se[l] ~1500	Br[m] ~1650	
5	Rb[n] 149			Sn[o] 1852				Xe[p] 5785
6	Cs[n] 252	Hg[q] 2460	Tl[q,r] 4800	Pb[q,s] 7300				

[a] H. S. Gutowsky and C. J. Hoffman, J. Chem. Phys. **19**, 1259 (1951); Ref. 7.
[b] E. B. Baker (personal communication). M. Weiner and R. West. J. Am. Chem. Soc. **85**, 485 (1963).
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[j] H. S. Gutowsky and D. W. McCall, J. Chem. Phys. **22**, 162 (1954); Ref. 11; J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, J. Am. Chem. Soc. **78**, 5715 (1956); H. Finegold, Ann. N. Y. Acad. Sci. **70**, 875 (1958).
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[l] H. E. Walchli, Phys. Rev. **90**, 331 (1953).
[m] By comparison with Cl in parallel Br and Cl studies in analagous compounds. Y. Masuda, J. Phys. Soc. Japan **11**, 670 (1956).
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[q] Ref. 9.
[r] H. S. Gutowsky and B. R. McGarvey, Phys. Rev. **91**, 81 (1953). B. N. Figgis, Trans. Faraday Soc. **55**, 1075 (1959). R. Freeman, R. Gasser, R. E. Richards, and D. Wheeler, Mol. Phys. **2**, 75, 357 (1959).
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commented on at the beginning of this section. But it can not be the cause of the large increases with Z of the chemical shift range for elements in a given group, as found in Table VI. We are left with the quantities $\langle 1/r^3\rangle_p$ and $\langle 1/r^3\rangle_d$ which to a first approximation are atomic properties and which one might expect to exhibit the appropriate periodicities.

$\langle 1/r^3\rangle$ and Spin–Orbit Interaction in Atoms

From atomic theory, one knows that *for the same atom*, the average value of r^{-3} over p (or d) electron wavefunctions decreases with quantum number n, that is, for example,

$$\langle 1/r^3\rangle_{3p} > \langle 1/r_3\rangle_{4p} > \langle 1/r^3\rangle_{5p} \cdots . \qquad (23)$$

Similarly, for different atoms with the same outer shell configuration, one expects $\langle 1/r^3\rangle_{np}$ and $\langle 1/r^3\rangle_{nd}$ *for the same shell* (*same* n) to increase with atomic number Z. However, the behavior of $\langle 1/r^3\rangle_{np \text{ or } d}$ versus atomic number Z, where n is now the quantum number of the outermost (valence) shell, cannot be arrived at readily by using the same kind of reasoning. In most of the calculations reported in the literature, $\langle 1/r^3\rangle$ is estimated by using Slater atomic orbitals. These give fair results for very light nuclei, but for most nuclei the values of $\langle 1/r^3\rangle$ obtained from the Slater orbitals are too small and the error gets worse with increasing Z. For example, $\langle 1/r^3\rangle_{5p}$ calculated for Xe ($Z=54$) with a Slater orbital is about a factor of 25 too small.

An experimental quantity which gives a quite direct

TABLE VII. Values of $\langle a_0^3/r^3\rangle_{np}$ and $\langle a_0^3/r^3\rangle_{nd}$ calculated from spin-orbit splittings in atoms.[a]

Atom	$3p$	$4p$	$5p$	$6p$	$7p$	$8p$	$9p$	n	nd
Al	1.27	0.20	0.084	0.046				3	0.009
Ga		3.48	0.48	0.19	0.099			4	0.016
In			5.71	0.79	0.30	0.15		5	0.036
Tl				11.81	1.54	0.58	0.28	6	0.074

[a] Spin-orbit splittings were obtained from Ref. 14.

measure of $\langle 1/r^3\rangle$ is the spin-orbit interaction, which is available from tables of atomic energy levels.[14] In Table VII are some values of $\langle a_0^3/r^3\rangle_{np}$ and $\langle a_0^3/r^3\rangle_{nd}$ calculated from the spin-orbit splitting, without relativistic correction. We note that for the same atom:

$$\langle 1/r^3\rangle_{3p} > \langle 1/r^3\rangle_{4p} > \langle 1/r^3\rangle_{5p} \cdots, \quad (24)$$

$$\langle 1/r^3\rangle_{np} > \langle 1/r^3\rangle_{nd}. \quad (25)$$

Also, for the same n, $\langle 1/r^3\rangle_{np}$ increases with Z for a given group in the table.

The equations used to calculate the values in Table VII were taken from Barnes and Smith,[15] who calculated $\langle a_0^3/r^3\rangle_{np}$ for the lowest lying p orbital of the outermost electrons, from spin-orbit splittings of various atoms from Li($2p$) to Bi($6p^3$). Their values are plotted in Fig. 1, with the following exceptions: For Sn more recent data are now available from Moore's tables,[14] Vol. III, from which we calculated $\langle a_0^3/r^3\rangle_{5p}=8.65$. This result was used to interpolate a new value for Sb. Also, the values of $\langle a_0^3/r^3\rangle_{np}$ for the rare gases were calculated from the spin-orbit couplings[16] and added to the figure.

It is evident from Fig. 1 that the periodicity in the range of chemical shifts parallels the periodicity in $\langle 1/r^3\rangle_{np}$. For d orbitals, one would expect the periodicity of $\langle 1/r^3\rangle_{nd}$ to be similar to that shown in Fig. 1 for p orbitals. However, the matter of the relative importance of the p and d electron contributions to $\sigma^{(2)}$ is somewhat more complex. The values given in Table VII for $\langle 1/r^3\rangle_{np}$ and $\langle 1/r^3\rangle_{nd}$, and the resultant inequality of Eq. (25), imply that the p-electron contribution to $\sigma^{(2)}$ must be at least one to two orders of magnitude larger than the d-electron contribution. However, the change in D_u can be larger than that in P_u. Therefore it may not be safe to neglect the d electrons for elements beyond the first row.

Finally, the scale relating $\langle a_0^3/r^3\rangle_{np}$ in Fig. 1 with the chemical shift ranges has, in effect, been calibrated by the calculations of $\sigma^{(2)}$ for F.[2,10] With allowance for the range in P_u, the magnitudes of $\langle a_0^3/r^3\rangle_{np}$ are compatible with the observed chemical shift ranges.

V. APPLICATIONS AND EXTENSIONS

The formulation given here is of general applicability to $\sigma^{(2)}$ for cases where *spd* hybridization is involved in the bonding orbitals of an atom. However, such applications are not necessarily very simple, even for monocoordinate atoms such as fluorine. This is shown by the evolution of our understanding of the fluorine shifts. The early measurements on the binary fluorides revealed that the ionic character of the M–F bond dominated the large range (625 ppm) of the fluorine

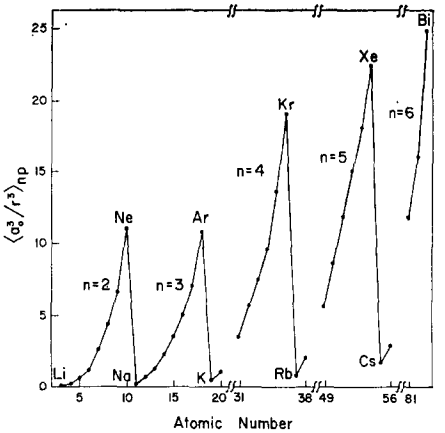

FIG. 1. The variation of $\langle a_0^3/r^3\rangle_{np}$ with atomic number, as calculated, mainly in Ref. 15, from the observed atomic spin-orbit splittings without relativistic correction.

shifts.[17] This observation led to the Saika and Slichter theoretical analysis[2] for $\sigma^{(2)}$ in terms of the unbalanced p electron distribution, P_u. They recognized that hybridization would effect the latter, but did not pursue the question inasmuch as the major trend of the experimental result could be explained by the fact that $P_u \cong P_u^0(1-i_F)$, where i_F is the ionic character of the M–F bond.

Extensive observations of the hundred-fold smaller ($\sim$5 ppm) fluorine shifts in substituted fluorobenzenes revealed the importance of double-bond as well as of ionic character and indicated the presence of an *ortho* effect.[18,19] This led to a corresponding refinement in the theory[10] for $\sigma^{(2)}$ to include the effects of s hybridization ($\sim$5%) as well as of p_π character ($\sim$10%) in the fluorine bonding orbital. Thus, in addition to Δ and $\langle 1/r^3\rangle_p$, there are at least three localized bond parameters, i, s, and p_π, which affect $\sigma_F^{(2)}$ by detectable amounts, at least in fluorobenzenes. Therefore, even if one supplements the observed isotropic chemical shift $\Delta\sigma$ with a measurement of the chemical shift anisotropy, η_σ, there are more unknowns than observed quantities and qualitative arguments have to be invoked to assess the relative importance of the smaller contributions to the chemical shifts.

One approach to this problem is to observe chemical shifts in a closely related series of compounds, for which there is good reason to believe that one or at most two of the bond parameters change to any major extent. This approach is largely the one followed for $\Delta\sigma_F$ in the *meta* and *para* substituted fluorobenzenes. Another possibility is the observation of the shifts for two or more nuclear species in the same compound, such that the shift for one nucleus may supply a reliable bonding parameter for the second. In the second paper of this

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[15] R. G. Barnes and W. V. Smith, Phys. Rev. **93**, 95 (1954).
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[17] H. S. Gutowsky and C. J. Hoffman, J. Chem. Phys. **19**, 1259 (1951).
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[19] V. D. Mochel, Ph.D. thesis, University of Illinois, 1960.

TABLE VIII. Values of $|\phi_s(0)|^2$, in atomic units, calculated from the corrected hyperfine splitting constants given by Knight[a] for a number of atomic species.

I	II	III	IV	VI
Li 0.21	Be 0.714		C (1.66)[b]	
Na 0.748	Mg 1.62	Al 2.41	Si 2.06	
K 1.105	Ca 2.02	Ga 7.16	Ge 4.92	Se 7.15
Rb 2.33	Sr 3.77		Sn 8.16	Te 11.0
Cs 3.87	Ba 6.11	Tl 18.9	**Pb** 13.8	

[a] Reference 24.
[b] This value, given in Ref. 23, was obtained in a different manner from the others and is not directly comparable with them.

series,[20] we have applied this procedure to the xenon fluorides, using the flourine shift as a measure of the Xe–F bond ionicity in calculations of the xenon shifts for various theoretical models of the bonding in the xenon fluorides. This leaves the hybridization of the xenon atomic orbitals as the *major* unknown factor governing the large observed xenon shifts and the trend in their values for the xenon fluorides.

The calculations for xenon illustrate in some detail the manner in which the formulation developed here can be applied. Similar applications can be made to other types of bonding situations and, in fact, it should be a quite straightforward extension to obtain general expressions for $\sigma^{(2)}$ for each of the conventional bond hybridization schemes commonly used, such as sp^2, sp^3, and dsp^3. In this connection, it should be mentioned that the expressions for $\sigma^{(2)}$ can be applied also to the transition metal ion complexes which have an even number of d electrons involved and which are diamagnetic. For example, when applied to Co^{+++} complexes (d^6), the expression for $\sigma^{(2)}$ gives the same result as Griffith[21] obtained by other means.

Electron Coupling of Nuclear Spins

Another related general phenomenon, for which there are more complex but similar periodicities to those for the chemical shifts, is the electron coupling of nuclear spins. The magnitude and also the range of values of the coupling constants exhibit a general increase with Z, but the problem is intrinsically more difficult than that for the chemical shifts. Part of the complexity is apparent in the sense that J_{ij}, the observed isotropic component of the coupling in cps between nuclei i and j is given as

$$J_{ij}=\gamma_i\gamma_j A_{ij}, \tag{26}$$

where γ_i and γ_j are the nuclear magnetogyric ratios and A_{ij} depends only upon the molecular electronic structure. Insofar as Eq. (26) is concerned, the values of γ for different nuclei are virtually random and the periodicities must be sought in the values of A_{ij} rather than J_{ij}. At this point the real complexities arise. First, A_{ij} involves the electron distributions in the vicinity of both nucleus i and j. Second, there are several terms contributing to A_{ij}, each of which is a different function of the molecular electronic structure, as in the case of $\sigma^{(1)}$, $\sigma^{(2)}$, and $\sigma^{(n)}$.

However, for directly bonded nuclei, at least when one is hydrogen, it appears that the contact term dominates A_{ij}[22,23]; that is

$$A_{\mathrm{MH}}\cong A_{\mathrm{MH}}{}^{C}=(C/\Delta)\,|\psi_{s\mathrm{M}}(0)|^2\,|\psi_{s\mathrm{H}}(0)|^2, \tag{27}$$

where C is a collection of constants and Δ is the appropriate average excitation energy. Furthermore, for each of the two nuclei in Eq. (27), the "contact function" can be expressed in a form similar to that for $\sigma^{(2)}$, namely

$$|\psi_s(0)|^2=p_{ss}\,|\phi_s(0)|^2, \tag{28}$$

where p_{ss} is the orbital population of the ns atomic orbital centered about the nucleus in question and involved in the M–H bond, and $|\phi_s(0)|^2$ is the ns wavefunction of the *atom*, evaluated at the nucleus. Therefore, one would expect A_{MH} to reflect the periodicity in $|\phi_{s\mathrm{M}}(0)|^2$ for the atoms. Values for the

TABLE IX. Internuclear coupling constants in the Group IV hydrides.

Compound	J_{MH} cps	A_{MH} cps $\hbar^2/\mu_0{}^2$	$\lvert\phi_{s\mathrm{M}}(0)\rvert^2$ a.u.	$\dfrac{A_{\mathrm{MH}}}{\lvert\phi_{s\mathrm{M}}(0)\rvert^2}$
$^{13}CH_4$	125[a]	16.0	(1.66)[b]	9.7
$^{29}SiH_4$	202.5[a]	32.7	2.06	15.8
$^{73}GeH_4$	87.8[c]	80.5	4.92	16.3
$^{119}SnH_4$	1931[d]	166	8.16	20.4
$^{207}PbH(CH_3)_3$	2379[d]	365	13.8	26.4

[a] Value cited in Ref. 23.
[b] See Table VIII.
[c] E. A. V. Ebsworth, S. G. Frankiss, and A. G. Robiette, (personal communication).
[d] N. Flitcroft and H. D. Kaesz, J. Am. Chem. Soc. **85**, 1377 (1963). J_{MH} does not appear to have been measured for PbH_4; however, methyl substitution has relatively little effect upon J_{MH} in the other Group IV hydrides so the value given for $^{207}PbH(CH_3)_3$ should be a good approximation to that in PbH_4.

[20] C. J. Jameson and H. S. Gutowsky, J. Chem. Phys. (to be published).
[21] J. S. Griffith, *The Theory of Transition-Metal Ions* (Cambridge University Press, Cambridge, 1961), p. 374.
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[23] C. Juan and H. S. Gutowsky, J. Chem. Phys. **37**, 2198 (1962).

latter are summarized for a number of elements in Table VIII. They were calculated directly from the "corrected" nuclear hyperfine interaction constants[24] $a(s)$ observed in atomic spectra. Knight[24] states that the values he gives for $a(s)$ should be accurate to better than 50% in most cases. At any rate, the same correction is applied to each degree of ionization so that while it may not be proper to compare values across the table, it is worthwhile to compare values down the table. (The last and next to the last column in Table VIII were probably overcorrected for ionization +4 and +6, respectively.)

It is apparent from Table VIII that the periodicities in $|\phi_s(0)|^2$ parallel those of $\langle 1/r^3\rangle_{np}$ given in Fig. 1. However, the experimental data available for A_{ij} do not permit as detailed a survey of periodicities in its magnitude as was possible for the chemical shifts. But the data for several Group IV hydrides provide at least some check on the validity of the approach incorporated in Eqs. (27) and (28). The results of such an analysis are summarized in Table IX. The values observed for J_{MH}, in cps, have been divided by $\gamma_M\gamma_H$ to give A_{MH} in units of cps $\hbar^2/\mu_0^2$, where μ_0 is the nuclear magneton.

These results for A_{MH} range from 16.0 for A_{CH} to 365 for A_{PbH}, somewhat over a twenty-fold increase. To a first approximation, the value of $|\psi_{sH}(0)|^2$ and the hybridization of the M atomic orbitals, sp^3, should be the same for all Group IV hydrides. Therefore, if our assumption that the contact term dominates A_{MH} is correct, the trend observed in A_{MH} should parallel the values for $|\phi_{sM}(0)|^2$. That this is very largely true is shown by the ratio of A_{MH} to $|\phi_{sM}(0)|^2$, given in the last column of Table IX, which exhibits a monotonic threefold increase from 9.7 for CH_4 to 26.4 for PbH_4 compared with the twenty-two-fold increase in A_{HH}. We have neglected thus far the dependence of Δ and the M–H bond polarity λ_{MH} upon Z_M. Both would tend to decrease with increasing Z_M in Group IV and this probably accounts for a significant part of the residual threefold increase in A_{MH}. Also, there is the possibility of noncontact contributions to A_{MH} which one would expect to become more important for the heavier atoms, with low-lying d orbitals. And again, as for $\sigma^{(2)}$, the polarization of core electrons should be considered. It is beyond the scope of this paper to treat the periodicities in A_{ij} in more detail. The example given does indicate that it may be fertile ground for further work. In fact, while this paper was in press, Smith[25] pointed out that in Group IV compounds of the type $X(CH_3)_4$ there is an approximately linear correlation between J_{XCH}/μ_X and n^3. Also, Reeves and Wells[26] have considered J_{XCH}/μ_X in these compounds as well as J_{XH}/μ_X in the hydrides and commented on the fact that both appear to be directly proportional to Z_X^2.

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[25] G. Smith, J. Chem. Phys. **39**, 2031 (1963).
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Combined Effects of Anisotropy in Nuclear Shielding and in Internuclear Coupling

In conclusion, we wish to point out a formal similarity between the combined effects of chemical shifts and electron coupling of nuclear spins in NMR and of the electron g value and nuclear hyperfine splitting in ESR spectra. The electron coupling of nuclear spins is of course a tensor interaction although Eqs. (26)–(28) deal only with the isotropic part, the average over random molecular orientations. The form of the internuclear interaction, $\mathbf{I}_i\cdot\mathbf{A}_{ij}\cdot\mathbf{I}_j$, is identical with that of the hyperfine interaction $\mathbf{I}\cdot\mathbf{a}\cdot\mathbf{S}$. Furthermore, the nuclear shielding tensor $\boldsymbol{\sigma}$ produces effects of the same form in NMR as does the $\mathbf{g}$ tensor in ESR spectra.

For example, in polycrystalline samples, the chemical shift anisotropy broadens the NMR absorption[27] in a manner equivalent to g anistropy in ESR spectra,[28] and this has been used to obtain the magnitude and sign of the chemical shift anisotropy. This broadening, in gauss, is of course directly proportional to $\eta_\sigma H_0$, the product of the anisotropy in the shielding and of the magnetic field at the nucleus. There should also be broadening from the anisotropy in the internuclear coupling tensor $\mathbf{A}_{ij}$. However, the latter has not yet been detected, probably because of its field-independent, relatively small magnitude. Single-crystal experiments, as for $\mathbf{g}$ and $\mathbf{a}$ in ESR, could provide complete information on the $\boldsymbol{\sigma}$ and $\mathbf{A}_{ij}$ tensors. The high-field, superconducting magnets now becoming available should prove useful in such experiments, especially in measurements of η_σ from the broadening of crystal powder spectra.

In the ESR spectra of solutions, the combined effects of anisotropy in $\mathbf{g}$ and in the hyperfine interaction can broaden the hyperfine components in a systematic manner which depends upon the magnitudes and signs of the anisotropies.[29] Such effects should, in principle, also occur in high-resolution NMR multiplets, though they would be much smaller because of the smaller magnitudes of the NMR anisotropies. Nonetheless, such effects may be large enough for detection in the NMR spectra of heavy nuclei which are directly bonded, for example in PbF_2. Their observation would be of interest, particularly as the absolute signs might thus be obtained relatively easily for the components of the internuclear coupling tensor.

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APPENDIX A: DIAGONAL ELEMENTS OF $\delta^{(2)}$ IN THE LCAO-MO FRAMEWORK

$$\sigma_{xx}^{(2)} = -(e^2\hbar^2/\Delta m^2c^2)\{\langle 1/r^3\rangle_p(p_{yy}+p_{zz}-p_{zz}p_{yy}+p_{yz}p_{zy})$$
$$+\langle 1/r^3\rangle_d\{3p_{z^2,z^2}+p_{x^2+y^2,x^2+y^2}+4p_{xz,xz}+p_{yz,yz}+p_{xy,xy}+\sqrt{3}(p_{x^2+y^2,z^2}+p_{z^2,x^2+y^2})$$
$$-3p_{z^2,z^2}p_{xz,xz}-p_{yz,yz}p_{xy,xy}-p_{xz,xz}p_{x^2+y^2,x^2+y^2}+3p_{z^2,xz}p_{xz,z^2}+p_{yz,xy}p_{xy,yz}+p_{xz,x^2+y^2}p_{x^2+y^2,xz}$$
$$+\sqrt{3}[-p_{xz,xz}(p_{x^2+y^2,z^2}+p_{z^2,x^2+y^2})+p_{xz,z^2}p_{x^2+y^2,xz}+p_{z^2,xz}p_{xz,x^2+y^2}+p_{xy,z^2}p_{yz,xz}-p_{yz,z^2}p_{xy,xz}+p_{xz,yz}p_{z^2,xy}-p_{z^2,yz}p_{xz,xy}]$$
$$+p_{xz,yz}p_{x^2+y^2,xy}+p_{yz,xz}p_{xy,x^2+y^2}-p_{x^2+y^2,yz}p_{xz,xy}-p_{xy,xz}p_{yz,x^2+y^2}\}\}. \quad \text{(A1)}$$

$$\sigma_{yy}^{(2)} = -(e^2\hbar^2/\Delta m^2c^2)\{\langle 1/r^3\rangle_p\{p_{xx}+p_{zz}-p_{zz}p_{xx}+p_{xz}p_{zx}\}$$
$$+\langle 1/r^3\rangle_d\{3p_{z^2,z^2}+p_{x^2+y^2,x^2+y^2}+p_{xz,xz}+4p_{yz,yz}+p_{xy,xy}+\sqrt{3}(p_{x^2+y^2,z^2}+p_{z^2,x^2+y^2})$$
$$-3p_{z^2,z^2}p_{yz,yz}-p_{yz,yz}p_{x^2+y^2,x^2+y^2}-p_{xz,xz}p_{xy,xy}+3p_{z^2,yz}p_{yz,z^2}+p_{yz,x^2+y^2}p_{x^2+y^2,yz}+p_{xz,xy}p_{xy,xz}$$
$$+\sqrt{3}[p_{yz,yz}(p_{x^2+y^2,z^2}+p_{z^2,x^2+y^2})-p_{yz,z^2}p_{x^2+y^2,yz}+p_{z^2,yz}p_{yz,x^2+y^2}+p_{xy,z^2}p_{xz,yz}-p_{xz,z^2}p_{xy,yz}+p_{yz,xz}p_{z^2,xy}-p_{z^2,xz}p_{yz,xy}]$$
$$+p_{xy,xz}p_{xz,x^2+y^2}-p_{xz,yz}p_{xy,x^2+y^2}+p_{x^2+y^2,xz}p_{yz,xy}-p_{yz,xz}p_{x^2+y^2,xy}\}\}. \quad \text{(A2)}$$

$$\sigma_{zz}^{(2)} = -(e^2\hbar^2/\Delta m^2c^2)\{\langle 1/r^3\rangle_p\{p_{xx}+p_{yy}-p_{xx}p_{yy}+p_{xy}p_{yx}\}$$
$$+\langle 1/r^3\rangle_d\{4p_{x^2+y^2,x^2+y^2}+p_{xz,xz}+p_{yz,yz}+4p_{xy,xy}-4p_{x^2+y^2,x^2+y^2}p_{xy,xy}-p_{xz,xz}p_{yz,yz}$$
$$+4p_{x^2+y^2,xy}p_{xy,x^2+y^2}+p_{xz,yz}p_{yz,xz}+2p_{x^2+y^2,xz}p_{xy,yz}+2p_{xz,x^2+y^2}p_{yz,xy}-2p_{x^2+y^2,yz}p_{xy,xz}-2p_{yz,x^2+y^2}p_{xz,xy}\}\}. \quad \text{(A3)}$$

APPENDIX B: DIAGONAL ELEMENTS OF $\delta^{(2)}$ IN THE VALENCE BOND FRAMEWORK

$$\sigma_{xx}^{(2)} = -(e^2\hbar^2/\Delta m^2c^2)\{\langle 1/r^3\rangle_p\{2\sum_{r=1}^{n}\eta_{ax}{}^2(1+\lambda_a{}^2)[(c_y{}^a)^2+(c_z{}^a)^2]-4\sum_{r>s}\sum\eta_{ax}{}^2\eta_{by}{}^2(1+\lambda_a{}^2)(1+\lambda_b{}^2)(c_z{}^ac_y{}^b-c_y{}^ac_z{}^b)^2\}$$
$$+\langle 1/r^3\rangle_d\{2\sum_{r=1}^{n}\eta_{ax}{}^2(1+\lambda_a{}^2)[3(c_{z^2}{}^a)^2+(c_{x^2+y^2}{}^a)^2+4(c_{xz}{}^a)^2+(c_{yz}{}^a)^2+(c_{xy}{}^a)^2+2\sqrt{3}c_{x^2+y^2}{}^ac_{z^2}{}^a]$$
$$-4\sum_{r>s}\sum\eta_{ax}{}^2\eta_{by}{}^2(1+\lambda_a{}^2)(1+\lambda_b{}^2)[\sqrt{3}(c_{xz}{}^ac_{z^2}{}^b-c_{z^2}{}^ac_{xz}{}^b)+(c_{xy}{}^ac_{yz}{}^b-c_{yz}{}^ac_{xy}{}^b)+(c_{xz}{}^ac_{x^2+y^2}{}^b-c_{x^2+y^2}{}^ac_{xz}{}^b)]^2\}\}. \quad \text{(B1)}$$

$$\sigma_{yy}^{(2)} = -(e^2\hbar^2/\Delta m^2c^2)\{\langle 1/r^3\rangle_p\{2\sum_{r=1}^{n}\eta_{ax}{}^2(1+\lambda_a{}^2)[(c_x{}^a)^2+(c_z{}^a)^2]-4\sum_{r>s}\sum\eta_{ax}{}^2\eta_{by}{}^2(1+\lambda_a{}^2)(1+\lambda_b{}^2)(c_x{}^ac_z{}^b-c_z{}^ac_x{}^b)^2\}$$
$$+\langle 1/r^3\rangle_d\{2\sum_{r=1}^{n}\eta_{ax}{}^2(1+\lambda_a{}^2)[3(c_{z^2}{}^a)^2+(c_{x^2+y^2}{}^a)^2+(c_{xz}{}^a)^2+4(c_{yz}{}^a)^2+(c_{xy}{}^a)^2-2\sqrt{3}c_{z^2}{}^ac_{x^2+y^2}{}^a]$$
$$-4\sum_{r>s}\sum\eta_{ax}{}^2\eta_{by}{}^2(1+\lambda_a{}^2)(1+\lambda_b{}^2)[\sqrt{3}(c_{z^2}{}^ac_{yz}{}^b-c_{yz}{}^ac_{z^2}{}^b)+(c_{yz}{}^ac_{x^2+y^2}{}^b-c_{x^2+y^2}{}^ac_{yz}{}^b)+(c_{xz}{}^ac_{xy}{}^b-c_{xy}{}^ac_{xz}{}^b)]^2\}\}. \quad \text{(B2)}$$

$$\sigma_{zz}^{(2)} = (e^2\hbar^2/\Delta m^2c^2)\{\langle 1/r^3\rangle_p\{2\sum_{r=1}^{n}\eta_{ax}{}^2(1+\lambda_a{}^2)[(c_x{}^a)^2+(c_y{}^a)^2]-4\sum_{r>s}\sum\eta_{ax}{}^2\eta_{by}{}^2(1+\lambda_a{}^2)(1+\lambda_b{}^2)(c_x{}^ac_y{}^b-c_y{}^ac_x{}^b)^2\}$$
$$+\langle 1/r^3\rangle_d\{2\sum_{r=1}^{n}\eta_{ax}{}^2(1+\lambda_a{}^2)[(c_{xz}{}^a)^2+(c_{yz}{}^a)^2+4(c_{xy}{}^a)^2+4(c_{x^2+y^2}{}^a)^2]$$
$$-4\sum_{r>s}\sum\eta_{ax}{}^2\eta_{by}{}^2(1+\lambda_a{}^2)(1+\lambda_b{}^2)[2(c_{x^2+y^2}{}^ac_{xy}{}^b-c_{xy}{}^ac_{x^2+y^2}{}^b)+(c_{yz}{}^ac_{xz}{}^b-c_{xz}{}^ac_{yz}{}^b)]^2\}\}. \quad \text{(B3)}$$