as a function of the correlation time $\tau_c$ indicated that this expectation was fulfilled.

Deguchi[47] interpreted his results on the ESR spectrum of the diphenyl nitric oxide radical in terms of Kivelson's theory which is, of course, equivalent to the one just outlined. As the spectrum was not completely resolved, Deguchi chose to calculate, from Kivelson's theory, the expected linewidths of the central three lines in each group. Here we may note that recently a better resolved spectrum has been obtained by Pannell.[61] In the case considered, the values available for the $I_z$ component of the nuclear spin of the nitrogen nucleus are 1, 0, $-1$. The six *ortho-* and *para*-protons in the phenyl rings will have $I_z$: $\pm 3$, $\pm 2$, $\pm 1$, 0, and the four *meta*-protons have $I_z$: $\pm 2$, $\pm 1$, 0. For the central three lines in each group, the half-widths calculated at the point of maximum slope are given in Table II. The observed linewidths, where available, are also given and it is seen that good agreement exists between the theoretically calculated values and the experimental results. It is to be noted that Deguchi's spectrum shows that the sharper lines, i.e., those with $M_{I(N)} = +1$ are at the low-field side of the spectrum.

We have already pointed out that the linear equation (41), and the linear term in Eq. (42), implies that the widths of lines with different $M$ values will depend on the sign of $g'_{\alpha\beta}T'^{(i)}_{\alpha\beta}$. For nitrogen atoms in aromatic systems there are reasons[58,60] for believing that $g'_{\alpha\beta}T'^{(i)}_{\alpha\beta}$ is negative. The lines in the spectrum with positive $M_I$ for the nitrogen atom should be narrower than those lines with negative $M_I$. In the case just discussed, the narrow lines with $M_I = +1$ lie at low field. It follows, therefore, that the isotropic hyperfine splitting constant for the nitrogen atom must be positive. A similar conclusion has been reached for the nitrogen atoms in other aromatic systems.[60,62]

[61] J. Pannell, Mol. Phys. **5**, 291 (1962).

[62] J. C. M. Henning and C. de Waard, Physica Letters **3**, 139 (1962).

## Discussion on Spin Resonance and Hyperfine Splitting

C. T. O'Konski and L. C. Allen, *Chairmen*

Goodman: Why isn't spin-orbit interaction included in the triplet splitting expression?

McWeeny: It would seem that examination of the $g$ values would be sufficient to show whether or not the spin-orbit coupling was important. The derivation of the spin Hamiltonian shows that the $g$ values involve matrix elements of the spin-orbit operator. When spin-orbit coupling is small the $g$ values are close to 2, and this is the usual case in hydrocarbons; the coupling may then be absorbed into empirical $g$ values and the electron spin–spin coupling calculated quite independently. Only in higher orders of perturbation theory would the spin-orbit coupling lead to spin–spin terms, and one might therefore expect such contributions to be negligible unless the $g$ values differed considerably from the spin-only value.

Goodman: It doesn't appear as if all of the spin-orbit interaction is included in the spin–spin Hamiltonian. When the atomic spin-orbit coupling vanishes as in the triplet state of a conjugated hydrocarbon, it is satisfactory to neglect the second-order term, but when there is persistence of atomic spin-orbit interaction (as in ketones, for example) then the interaction between the triplet and singlet probably becomes important to the splitting.

McWeeny: This comment concerns the general question of how the empirical constants in the spin Hamiltonian can be understood in terms of the electronic wave function. The full Hamiltonian is

$$\mathcal{H} = \mathcal{H}_0 + (\text{terms involving electron and nuclear spins}) ,$$

where $\mathcal{H}_0$ is a spin-independent electronic Hamiltonian, whose eigenfunctions are made the basis of a perturbation calculation. The remaining terms include interactions between electron and nuclear spins and the magnetic field, spin-orbit coupling, contact couplings, and dipole–dipole couplings. It can then be shown [M. H. L. Pryce, Proc. Phys. Soc. (London) **63**, 25 (1950)] that, to a certain approximation, the eigenvalues of the $\mathcal{H}$ coincide with those of a *spin* Hamiltonian, $\mathcal{H}_{\text{spin}}$, operating within a manifold of electron-nuclear spin states and containing constants which are determined by the electronic wave function. These constants are in fact expressible in terms of the spinless components of certain one- and two-electron density matrices. If we write the transition density matrices between electronic states $\Psi_\kappa$, $\Psi_\lambda$ as

$$\rho_1(\kappa\lambda|x_1;x_1') = P_1(\kappa\lambda|\overset{+}{r}_1;\overset{+}{r}_1')\alpha(s_1)\alpha^*(s_1') + P_1(\kappa\lambda|\overset{+}{r}_1;\overset{-}{r}_1')\alpha(s_1)\beta^*(s_1') + \cdots ,$$

$$\rho_2(\kappa\lambda|x_1x_2;x_1'x_2') = P_2(\kappa\lambda|\overset{+}{r}_1\overset{+}{r}_2;\overset{+}{r}_1'\overset{+}{r}_2')\alpha(s_1)\alpha(s_2)\alpha^*(s_1')\alpha^*(s_2') + \cdots ,$$

then all the matrix elements which appear are determined by a small number of combinations of the spinless components (the $P$'s). These new density functions [R. McWeeny and Y. Mizuno, Proc. Roy. Soc. (London) **A259**, 554 (1961)] all have a useful physical interpretation, though attention has so far been confined mainly to the spin density. With an obvious abbreviation for the spinless components, $P_1(\kappa\lambda|r^+_1;r^+_1') = (+\ +)$ etc., it is found that for states which are spin eigenfunctions $\rho_1$ and $\rho_2$ have only two and six nonzero components, respectively. In a given state ($\kappa = \lambda$) the sum and difference of the $\alpha$ and $\beta$ densities are

$$P_1 = (+\ +) + (-\ -) \text{ (the electron density)}$$

$$Q_1 = (+\ +) + (-\ -) \text{ (the spin density)} .$$

The latter (excess of $\alpha$-spin density over $\beta$-spin) integrates over all space to give $2M_s$ and the normalized density introduced by McConnell is thus $\rho_s = Q_1/2M_s$. The first *two*-electron function is

$$P_2 = (++|++) + (+-|+-) + (-+|-+) + (--|--) \text{ (the pair function)} ,$$

which is the sum of the probabilities for the four possible spin configurations of the electrons in two selected volume elements. The remaining density functions [R. McWeeny and Y. Mizuno, Proc. Roy. Soc. (London) **A259**, 554 (1961)] include a spin-coupling density $Q_c$, whose integral over all positions of both volume elements yields the expectation value of

$$\sum_{i,j=1}^{N} \mathbb{S}(i)\cdot\mathbb{S}(j) ,$$

and a function $Q_{c,a,}$ which measures the anisotropy in the spin coupling. Each density function determines a certain type of physical effect: thus, for example, $Q_1$ determines electron-nuclear hyperfine couplings (both contact and dipole–dipole) and the spin-orbit coupling (which is also linear in the electron spins); while $Q_{c,a,}$ determines [R. McWeeny and Y. Mizuno, Proc. Roy. Soc. (London) **63**, 25 (1950); R. McWeeny, J. Chem. Phys. **34**, 399 (1961)] the electron–electron dipole coupling. It is suggested that more attention be given to density functions of this kind, in efforts to understand and relate the various spin-coupling effects which are being revealed by present electron and nuclear magnetic resonance experiments.

LÖWDIN: In the current theoretical literature about hyperfine splitting and the question of the spin densities at an atomic nucleus, there is a great deal of controversy and confusion coming from the fact that one really does not know how to calculate properly other properties than the energy. Since the Schrödinger equation $\mathfrak{H}\Psi = E\Psi$ defining the stationary states of interest in the problem usually cannot be solved in closed form, one has to be satisfied if the solution can be reached by limiting procedures of the type

$$\lim_{n\to\infty} \Psi_n = \Psi , \qquad \lim_{n\to\infty} E_n = E . \tag{1}$$

All wave functions are assumed to be normalized to unity. The main question now is whether the expectation values $F_n = \langle\Psi_n|F|\Psi_n\rangle$ of a specific physical quantity $F$ converge towards the correct value $\langle F\rangle$ at the same time as the energy does. That this is not obvious has been emphasized before [P. O. Löwdin, Ann. Rev. Phys. Chem. **11**, 111 (1960)].

It should be first observed that the first relation in (1) to a certain extent depends on the second. Introducing the overlap integrals $S_n = \langle\Psi|\Psi_n\rangle$ and choosing the phases so that they become real and positive, one has $\int |\Psi_n - \Psi|^2(dx) = 2\,(1 - S_n)$. For the ground state, this error integral is maximized by Eckart's criterion [C. Eckart, Phys. Rev. **36**, 877 (1930); cf. B. A. Lengyel, J. Math. Anal. Appl. **5**, 451 (1962)]

$$1 - S_n^2 \leq \frac{\langle\Psi_n|\mathfrak{H}|\Psi_n\rangle - E}{E_I - E} , \tag{2}$$

where $E_I$ is the energy of the first excited state. In order to treat the quantity $F$, which is represented by an Hermitian operator, we observed the validity of the identity [P. O. Löwdin, Ann. Rev. Phys. Chem. **11**, 111 (1960)]:

$$\langle\Psi_n|F|\Psi_n\rangle - \langle\Psi|F|\Psi\rangle \equiv 2\,(1 - S_n^2)^{\frac{1}{2}}\,\mathrm{Re}\,(\chi_-|F|\chi_+)\,, \tag{3}$$

where $\chi_\pm = (\Psi_n \pm \Psi)\,(2 \pm 2S_n)^{-\frac{1}{2}}$ are two orthonormal functions in the plane of the vectors $\Psi_n$ and $\Psi$. It is obvious that, if $F$ is a bounded quantity, then $\langle F\rangle_n - \langle F\rangle$ goes to zero as $[E_n - E]^{\frac{1}{2}}$, i.e., as a first-order quantity in accordance with the variation principle. Most physical properties are not represented by bounded operators, but it may be shown that the limiting procedure for $\langle F\rangle_n$ is well behaved as long as $F$ is bounded within the subspace spanned by the functions $\Psi$, $\Psi_1, \Psi_2, \cdots \Psi_n \cdots$.

The limiting procedure is often obtained by means of the Ritz expansion method applied to truncated sets which are then extended so that they tend to be complete. The convergence properties of quantities of the type $F = r^p$ have been studied in this connection by Faulkner and Nordling [S. Faulkner and J. Nordling, Technical Report No. 33, 1962, Quantum Theory Project, University of Florida, Gainesville, Florida (unpublished)] for various simple Hamiltonians, and they point out that the convergence is well behaved as long as the operators considered are not more unbounded than the Hamiltonian itself.

Let us now return to the spin density $1/2(\rho+ - \rho -)$ which may be considered as the expectation value of the operator

$$\sum_{i=1}^{N} s_z(i)\delta(r_i - r)\,. \tag{4}$$

Considered as a "point property," this operator containing $\delta$ functions are certainly not bounded. However, if we integrate the spin density over $r$ over a small volume, say, the volume of the nucleus involved, this integrated density is always bounded and will then be well behaved and converge simultaneously with the energy.

A detailed discussion of the error limits for the electron density, the spin density, and the atomic form factors has recently been given by Redei. [L. B. Redei, Phys. Rev. **130**, 420 (1963).] A somewhat different treatment of the spin density has also been given by Sasaki. [F. Sasaki and K. Ohno, Uppsala Quantum Chemistry Group, Technical Note No. 90, 1962, Uppsala University, Uppsala, Sweden (unpublished).]

McWeeny: In some recent work [R. McWeeny and B. T. Sutcliffe, Mol. Phys. (to be published); B. T. Sutcliffe (to be published)] the spin density in the $NH_2$ radical has been calculated nonempirically, with results which may be of some interest in this discussion. Two approaches were used: (i) a configuration interaction method; and (ii) the unrestricted Hartree–Fock method, with and without projection to a pure spin state. All calculations were performed with two alternative choices of orbital basis, namely, the Slater orbitals used by Duncan in his ammonia calculation and the Hartree orbitals used by Kaplan. Since all the necessary integrals were available for $NH_3$, it was decided to make a test calculation with the ammonia H–N–H angle (106°47′) instead of the $NH_2$ angle of 103°23′. It was hoped that this would at least give the main features of the spin-resonance spectrum, besides permitting a careful comparison of theoretical methods.

In the configuration interaction calculation, the basic approximation was an antisymmetrized product with factors referring to inner shell, lone pair, bond pairs, and the odd $\pi$-electron: these localized functions were constructed by methods described elsewhere. [R. McWeeny and K. Ohno, Proc. Roy. Soc. (London) **A255**, 367 (1960).] The "excited" configurations were formed by introducing the first triplet states of each bond, coupling these to the odd electron to give the doublet symmetry of the ground state. The hyperfine constants, which are then determined by a singlet–triplet transition-spin density for each bond, are found to be in quite good agreement with experimentally inferred values (in both magnitude and sign).

The unrestricted Hartree–Fock calculation, which follows standard lines, gives somewhat less satisfactory values. On annihilating the quartet contamination, to obtain an almost pure doublet function, there is some improvement. This suggests that projection may be worthwhile as Löwdin

suggests, even *after* the variational calculation, although statements to the contrary have been made by Marchall and others. Ideally, of course, the projection would be made *before* determining the best orbitals: but this leads to very great computational difficulties. In the configuration interaction calculation no such difficulties are encountered.