manner. We believe, however, that every class of catalysts, metals, acidic oxides, etc., probably has a member of the class that approaches being a poor catalyst in the right way for infrared detection of intermediates to be feasible. For these, infrared studies under dynamic conditions approximating those used in conventional catalytic studies can be coupled with tracer techniques and traditional studies to yield a detailed picture of the reaction sequence.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of part of this research. This research was also aided by funds from the National Science Foundation under Grant GP 34034X.

Effects of Molecular Reorientation on Electron Spin Resonance Spectra

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Received August 4, 1972

It has now become commonplace for chemists to observe and measure a variety of processes—conformation changes, rotational and translational diffusion, chemical reactions—by their effects on magnetic resonance spectra. In many instances increasing rates are accompanied by narrowing of spectral responses. To a senescent spectroscopist nurtured on the doctrine that enhancement of spectral resolution in dense media was to be sought by freezing out troublesome molecular motions through use of low temperatures and high viscosities, there is a sense of delight not only because the doctrine is wrong but because examination of its failures has shown how analysis of spectra can often reveal features of the motions not previously experimentally accessible.

Some of the ruminations in the succeeding pages may appear to be naive; they represent my attempts to get an intuitive grasp of the phenomena. "Intuitive grasp" here means the ability to obtain qualitative relations without lengthy formal calculations. In this article I discuss only a few applications of the ideas to some of the effects of rotational diffusion on magnetic resonance spectra, in particular the way in which the dipole–dipole interaction responds to such rotational motion. The reader who seeks mathematically satisfying rigorous treatments of the phenomena is referred to the recent work listed in the first reference[1] and to the earlier works cited in them.

We start with a description of the dipole–dipole interaction and its application to a familiar case—the proton magnetic resonance spectra of water. Although the calculations are usually carried out through use of the Hamiltonian form of the interaction, we use the dipolar field because of its readier conceptualization.

Consider a dipole μ situated at the center of a sphere. The field at each point on the sphere depends in direction and magnitude on the orientation of its radius vector relative to the dipole. At each orientation the magnitude of the field is inversely proportional to the cube of the radius. The angular dependence may be represented by the variation on the spherical surface. The field at each orientation lies in the plane defined by the direction of the dipole and the radius vector. Its component parallel to the dipole at a point whose radius vector makes angle θ with the dipole is proportional to $\frac{1}{3} + \cos 2\theta = \frac{2}{3}(3\cos^2 \theta - 1)$; the component perpendicular to the dipole varies as $\sin 2\theta = 2 \sin \theta \cos \theta$. The energy of interaction, E_{12}, between two dipoles is the negative of the scalar product of the field at one of the dipoles with its dipole moment; *i.e.*, $-E = \mathbf{H}_1(r_2)\cdot\mu_2 = \mathbf{H}_2(r_1)\cdot\mu_1$, where $\mathbf{H}_1(r_2)$ is the field at position of dipole μ_2 produced by dipole μ_1 and $\mathbf{H}_2(r_1)$ is the field at dipole μ_1 produced by μ_2. The familiar Hamiltonian form of the interaction exhibits its symmetry

$$H_{12} = \frac{1}{r^3}\left[\mu_1\cdot\mu_2 - \frac{3(\mu_1\cdot\mathbf{r})(\mu_2\cdot\mathbf{r})}{r^2}\right]$$

where r is the distance between dipoles and $\mathbf{r}$ the vector joining them. The interaction may be expanded in products of components of the two dipole vectors; the coefficients form a tensor of zero trace.

The dipolar interaction described above is sufficient to account for the effects of rotation in many instances in which identical spins in equivalent environment interact. Examples are the proton resonance in water and the electron spin resonance in a

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(1) M. Fixman, *J. Chem. Phys.*, **48**, 534 (1968); H. Sillescu and D. Kivelson, *ibid.*, **48**, 3493 (1968); R. G. Gordon, *Advan. Magn. Resonance*, **3**, 1 (1969); H. Silliscu, *J. Chem. Phys.*, **54**, 2110 (1971); J. H. Freed, G. V. Bruno, and C. Polnaszek, *ibid.*, **55**, 5270 (1971); R. M. Lynden-Bell, *Mol. Phys.*, **22**, 837 (1971).

ground-state triplet. In other cases in which unlike spins or like spins in different average environments interact, isotropic interactions, *i.e.*, those which are independent of orientation of interspin vector, must be included. Although their physical origin is sometimes complicated, their contribution to the interaction is simple; it has the form $A\mu_1 \cdot \mu_2$ where A is a constant which depends on the nature of the interaction. When both types of interactions are present, they are conveniently included in a single tensor; the trace of this tensor is $3A$. One example of a dipole–dipole interaction in which both the isotropic and anisotropic contributions are important is that of the nitroxide free radicals used by McConnell[2] as spin labels. The interaction in them is between the electronic magnetic moment and a nitrogen nuclear moment.

Appreciation of the numerical magnitudes of the effective fields in various situations is helpful in understanding the phenomena. The dipolar field at a distance of 1 Å from an electron spin is about 10^4 G; at 1 Å from a proton about 15 G. The effective field at a nucleus associated with its isotropic interaction with another nucleus is generally less than 1 G, but the field at a nucleus associated with its isotropic interaction with an electron spin may be several hundred thousand gauss. Experiments are carried out at external fields lying between zero and about 5×10^4 G; many features of the phenomena depend on the relative magnitudes of the external and internal fields.

One of the earliest and still most instructive studies of the effects of the dipole–dipole interaction on magnetic resonance was Pake's[3] work with calcium sulfate dihydrate crystals. Because all internal magnetic fields are small (~15 G) relative to the external field (6800 G) only the component of internal field parallel to the external field need be considered; the effective field at each nucleus is $H_0 \pm (\mu/r^3)(3 \cos^2 \theta - 1)$, where θ is the angle between proton–proton vector and the external field H_0. Because the Hamiltonian is invariant to exchange of the nuclei, the spin eigenstates are triplet and singlet; transitions between singlet and triplet being forbidden, we need consider only the transitions within the triplet manifold. The energy intervals between adjacent states are not equal; consequently, the two allowed transitions are not coincident. Each orientation produces a pair of peaks symmetrically displaced from the position of the peak for the single nucleus; the displacement varies as $3 \cos^2 \theta - 1$. The spectrum of a random array of nonrotating molecules is obtained by summing the contributions from the individual orientation. Pake's measured spectra for oriented crystals and from powdered samples are shown in Figure 1. They are completely accounted for by the elementary considerations described above.

The spectrum of the powdered sample extends over a frequency range of some 50,000 Hz; the interval between the members of the doublet from a single orientation undergoes a similar variation as the orientation is varied relative to the external field. The extraordinary feature of the phenomena, characteristic of many of the motional effects in magnetic resonance, is the wide difference between the spectrum of rapidly tumbling water molecules—a single sharp line with breadth of only a few tenths hertz—and the spectrum of randomly oriented but nontumbling molecules in the powdered crystals.

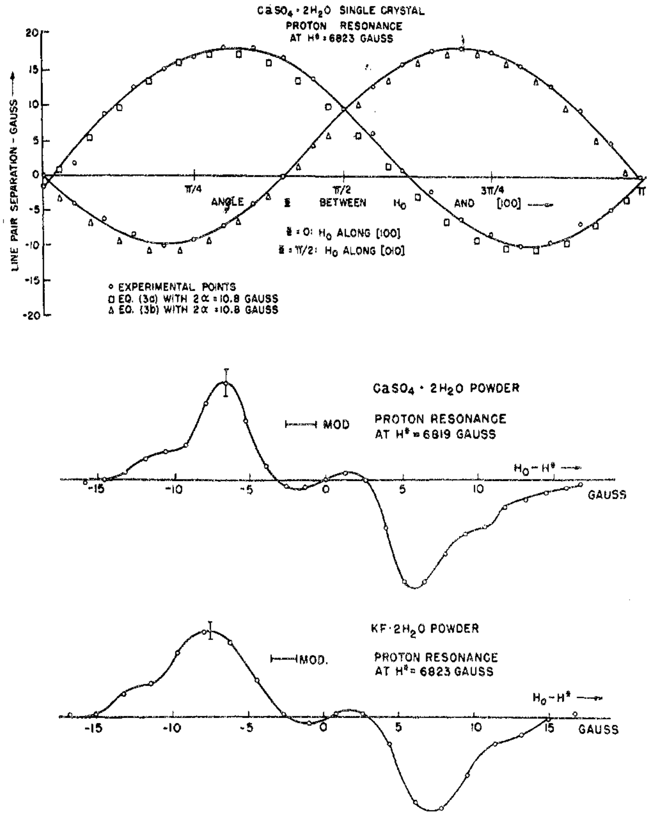

Figure 1. (Upper) Angular dependence of positions of proton resonances in $CaCO_4 \cdot 2H_2$. (Lower) Derivative of absorption *vs.* field in powdered $CaSO_4 \cdot 2H_2O$ and $KF \cdot 2H_2O$ (Courtesy of Dr. G. E. Pake).

A related example—almost identical in the nature of the physical phenomena, but with very different numerical magnitudes of the parameters—is found in electron spin resonance spectra of systems containing pairs of unpaired electrons. I discuss this example—taken from the work of James Norris[4]—because the numerical values of the parameters have permitted convenient study of the way in which the line shape changes with molecular reorientation (the example is perhaps too simple because it does not include contribution of nonadiabaticity, which will be discussed later). Norris studies a number of chemically tractable systems containing two unpaired electrons; they are formed by joining a pair of radical ions by two monopositive metal ions or a single dipositive ion. An example of the former is the combination of two fluorenone radical ions with two sodium ions; of the latter, two dipyridyl anions joined by a beryllium ion. In rigid media the esr spectra in the region of the free electron resonance are very similar in shape to Pake's proton spectrum of powdered calcium sulfate dihydrate. One outstanding difference appears at half the normal resonant field where a single sharp

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(2) For a recent work which includes references to many of the earlier ones see P. Duvaux and H. McConnell, *J. Amer. Chem. Soc.*, **94**, 4475 (1972).

(3) G. E. Pake, *J. Chem. Phys.*, **16**, 327 (1948).

(4) J. Norris, Ph.D. Thesis, Washington University, 1968; J. Norris and S. I. Weissman, *J. Phys. Chem.*, **73**, 3119 (1969).

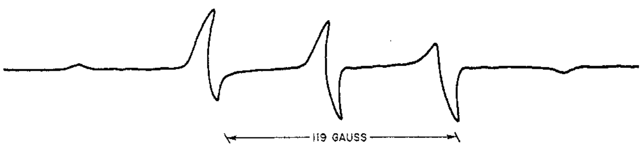

Figure 2. Derivative of electron spin absorption *vs.* field in the dimer of sodium fluorenone ketyl.

resonance is observed. It occurs because the internal field, ~100 to 500 G, is not negligible compared with the external one of ~3000 G. Although the interval between the lowest and highest levels of the triplet manifold is independent of the molecular orientation to first order, the deviations of orientations of the spins from parallelism with the external field are sufficient to permit observation of the "$\Delta m = 2$" or "half-field" resonance.[5] The "allowed" $\Delta m = 1$ part of the spectrum of the randomly oriented rigid array extends over about 10^9 Hz. The forbidden $\Delta m = 2$ part with integrated intensity only about one-thousandth of the allowed part is nevertheless easily observed because of its narrowness.

We now proceed to an examination of changes of the spectra described above with molecular reorientation. The discussion is based mainly on Norris'[4] study. Except for differences in time scale, the behavior of the nuclear two spin systems are similar. The spectrum of the electronic triplet in rigid medium spans a frequency range of about 10^9 Hz and requires correspondingly more rapid rotational motion for production of changes in line shape than does the nuclear system. Consider first the two extremes of the spectrum. In rigid medium the spectrum of fluorenone dimer is exhibited in Figure 2.[6] With decreasing viscosity of the medium the spectrum changes smoothly toward the liquid one—a single sharp resonance at the normal resonant frequency. A familiar description of the resonance in the liquid runs about as follows: All the space-dependent parts of the dipolar Hamiltonian average to zero over an isotropic distribution. Therefore they make no important contributions in the liquid. But they also average to zero (ensemble average) in the isotropic rigid distribution. The difference lies in the way in which the average is taken. In the limit of rapid rotation the wave function of each molecule is taken to represent a spherically symmetrical distribution of orientation, similar to an s state of an atomic system. Expectation values of all space-dependent parts of the dipolar tensor vanish. Such a description yields a correct description of positions of absorption peaks but fails to account for their shapes. The procedures currently in use to account for the line shapes involve making a guess as to the nature of the motion and calculating its effect on the spectrum. The nature of the guess is usually dictated by the guesser's prejudices and the ease with which the guess may be parametrized and incorporated into a calculation.

One illuminating way of displaying the connection between the spectrum and the motion has now become familiar through the use of Fourier transform spectroscopy. The ordinary magnetic resonance absorption spectrum is the Fourier transform of the time dependence of the magnetization after application of an appropriate pulse. Clearly, molecular motions of the system which affect its magnetization will also affect the time dependence of the magnetization and hence the spectrum. Norris calculated by numerical methods, to an adequate approximation, the effect of assumed motions on the spectrum. He first tried a kind of motion for which the computations are easiest: the time evolution of the magnetization for the so-called "strong collision," or "all-site" model, a model in which the motion occurs in very rapid finite jumps with resting periods between jumps, jumps of all magnitude being equally probable. The model fails: no choice of jump rate reproduces the shape of the spectrum in the region in which the spectrum has not collapsed to a single sharp peak. But a random walk model in which frequent small jumps between nearby sites occur (large jumps being excluded) permits fitting of each spectral shape by a single rotational rate. Representative spectra and the rates associated with them are shown in Figure 3.

Because of the numerical magnitudes of the various effects operating in Norris' study the interpretation is particularly simple. The internal fields were in no case greater than one-tenth of the external field, so that to a moderately good approximation the spin eigenstates are independent of molecular orientation. Only their energy eigenvalues, and correspondingly the resonant frequencies, change with the motion. Hence Norris' solution corresponds to a frequency modulation model,[7] the frequency modulation being produced by the random walk among the orientations. Another effect—the production of transitions between eigenstates by fluctuating components of the dipolar field—is not important in this case because the motions are not rapid enough to contain appreciable amplitude at the resonant frequency.

Although Norris' analysis, despite its approximations, accounts for the part of the spectrum near the electron spin resonant frequency, it is incapable of accounting for the half-field or $\Delta m = 2$ region. With increasing rotational rate the $\Delta m = 2$ resonance, which is narrow in the rigid medium, broadens monotonically. The behavior of the two sets of resonances which occur in the same manifold of three spin state may seem mutually contradictory, the $\Delta m = 1$ transition becoming narrow as the $\Delta m = 2$ transition becomes broad. Assignment of a breadth to each of the three spin levels in the fluid solution is not a satisfactory way of describing the spectral behavior, for the breadth of the $\Delta m = 2$ transition in the fluid region would require that at least one of the levels be broad and the narrowness of the $\Delta m = 1$ transitions requires that none be broad. We may resolve the difficulty by treating the spin system as subject to a time-dependent Hamiltonian, in which case it has no stationary states. The allowed transitions are frequency modulated in a random manner; the spectrum[7] is a sharp peak with broad but weak tails extending over the range of frequencies covered by the rotational motion. The $\Delta m = 2$ transition gains all its intensity from departures from perfect

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(5) J. H. van der Waals and M. S. de Groot, *Mol. Phys.*, **2**, 333 (1959).

(6) N. Hirota and S. I. Weissman, *Mol. Phys.*, **5**, 537 (1967).

(7) P. W. Anderson, *J. Phys. Soc. Jap.*, **9**, 316 (1954).

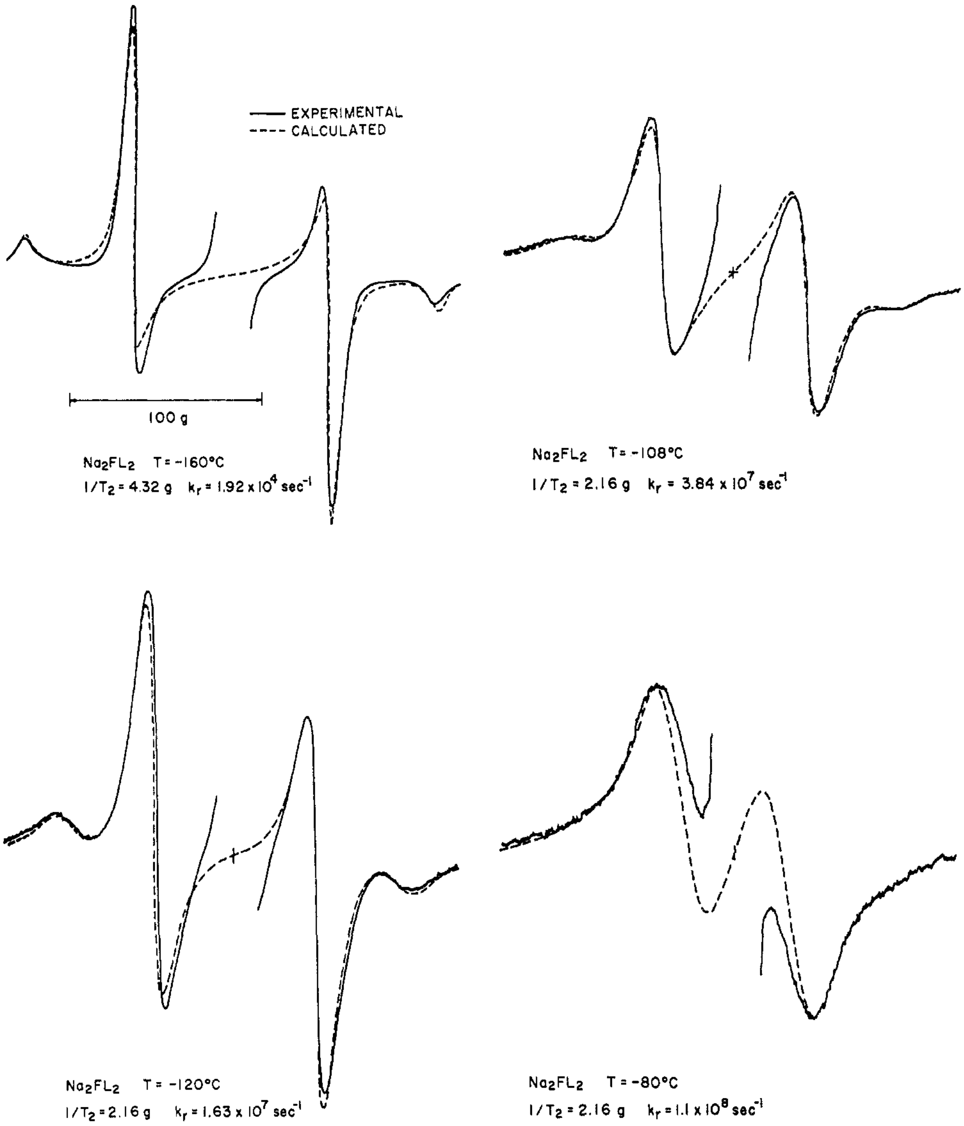

Figure 3. Spectra of dimer of sodium fluorenone ketyl at different viscosities; calculated spectra for random walk model.

alignment of spins along the external field; the spectrum is amplitude modulated as the molecules rotate. It consists of side bands with frequency spread of the order of the rotational frequency.

In Norris' work the rotational reorientation was viewed as a succession of jumps between resting periods, a model naturally suggested by the way in which he carried out the experiments—observation of the spectra in dense media whose properties varied from rigidity to fluidity. At the other extreme is the study by Kivelson and Schaafsma[8] of the spectra of the radical $(CF_3)_2NO$ in the gas phase. In dilute solution in an inert liquid the radical has a well-resolved spectrum; at low pressure the pure gaseous radical has only a broad unresolved spectrum. Addition of an inert foreign gas at high pressure produces a resolved liquid-like spectrum. The spectrum in the dilute gas arises from molecules occupying well-defined rotational eigenstates. The contribution of the dipole–dipole interaction does not vanish for a molecule in one of its rotational eigenstates (except for the symmetric nonrotating state), but in molecules in a superposition of such states with rapidly varying amplitudes and phases the dipole–dipole interaction does vanish. High rotational angular momentum alone does not produce liquidlike behavior; frequent interruptions of the motion accompanied by changes in orientation of angular momentum does. (For a diatomic molecule rapid transitions among the *m* values corresponding to a given total angular momentum suffice to average out the dipolar interaction.)

The Kivelson–Schaafsma experiments would then suggest as model for reorientation in liquids changes in direction and magnitude of the angular momentum. Recently Kivelson and Keyes[9] have presented a unified description of molecular reorientation which includes both the limiting cases—reorientation between resting periods and reorientation of angular momentum—in a single conceptual scheme.

In the cases discussed in the preceding paragraphs the spectrum in the limit of rapid motion consists of sharp responses at frequencies which are the averages over those which are observed for random distribution of fixed orientations. May we assume that for all cases of motionally averaged spectra the ob-

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(8) T. J. Schaafsma and D. Kivelson, *J. Chem. Phys.*, 49, 5235 (1968).

(9) D. Kivelson and T. Keyes, *J. Chem. Phys.*, 57, 4509 (1972).

Chart I

$$\begin{array}{cccc}
\boldsymbol{\uparrow}\uparrow & \boldsymbol{\uparrow}\downarrow & \boldsymbol{\downarrow}\downarrow & \boldsymbol{\downarrow}\uparrow \\
\frac{3A}{4}(1 - 2\cos^2\theta) + \frac{g\beta H}{2} & -\frac{3A}{2}\sin\theta\cos\theta\, l^{i\phi} & 0 & 0 \\
-\frac{3A}{2}\sin\theta\cos\theta\, l^{-i\phi} & -\frac{3A}{4}(1 - \cos^2\theta) + \frac{g\beta H}{2} & 0 & 0 \\
0 & 0 & \frac{3A}{4}(1 - 2\cos^2\theta) - \frac{g\beta H}{2} & -\frac{3A}{2}\sin\theta\cos\theta\, l^{i\phi} \\
0 & 0 & -\frac{3A}{2}\sin\theta\cos\theta\, l^{-i\phi} & -\frac{3A}{4}(1 - 2\cos^2\theta) - \frac{g\beta H}{2}
\end{array}$$

served frequencies may be obtained by a similar averaging process? The answer is no as we demonstrate for two cases: one in which the spectrum in the absence of motion is independent of orientation in an external field and another in which in the absence of any external static field the rigid and motionally narrowed spectra are completely different.

Suppose we could produce a free radical in which the relative signs and magnitudes of the isotropic and anisotropic interactions between electron and nucleus are given by the following tensors.

$$\tilde{\mathbf{A}}_{\text{isotropic}} = \begin{bmatrix} A & 0 & 0 \\ 0 & A & 0 \\ 0 & 0 & A \end{bmatrix}$$

$$\tilde{\mathbf{A}}_{\text{anisotropic}} = \begin{bmatrix} -4A & 0 & 0 \\ 0 & 2A & 0 \\ 0 & 0 & 2A \end{bmatrix}$$

$$\tilde{\mathbf{A}}_{\text{total}} = \begin{bmatrix} -3A & 0 & 0 \\ 0 & 3A & 0 \\ 0 & 0 & 3A \end{bmatrix}$$

Such a combination represents the case in which the magnitude of the internal field at the nucleus (but not its direction) is independent of molecular orientation.

The Hamiltonian matrix when the external field is large compared with the internal field at the electron but small compared with the internal field at the nucleus is given in Chart I, where θ and ϕ are the polar angles of the external field H relative to the principal molecular axes; g and β are the magnetogyric ratio and Bohr magnetion of the electron; and the heavy and light arrows represent the electron and nuclear spin states. The nucleus has spin ½. The eigenvalues of the Hamiltonian are independent of orientation. They are $\pm g\beta H/2 \pm 3A/4$. But the eigenfunctions depend on orientation: They are

$$\cos\theta\,|\boldsymbol{\uparrow}\uparrow\rangle - \sin\theta\,|\boldsymbol{\uparrow}\downarrow\rangle \qquad E = \frac{g\beta H}{2} + \frac{3A}{4}$$

$$\sin\theta\,|\boldsymbol{\uparrow}\uparrow\rangle + \cos\theta\,|\boldsymbol{\uparrow}\downarrow\rangle \qquad E = \frac{g\beta H}{2} - \frac{3A}{4}$$

$$\cos\theta\,|\boldsymbol{\downarrow}\downarrow\rangle - \sin\theta\,|\boldsymbol{\downarrow}\uparrow\rangle \qquad E = -\frac{g\beta H}{2} + \frac{3A}{4}$$

$$\sin\theta\,|\boldsymbol{\downarrow}\downarrow\rangle + \cos\theta\,|\boldsymbol{\downarrow}\uparrow\rangle \qquad E = -\frac{g\beta H}{2} - \frac{3A}{4}$$

(The spin orientations are given in the laboratory frame). Consider a fixed molecule with $\theta = 0$, *i.e.*, principal axis parallel to the field, in the eigenstate $|\boldsymbol{\uparrow}\uparrow\rangle$. Turn the molecule slowly in this field. The nuclear spin eigenstate retains its orientation relative to the internal field; at $\theta = \pi/2$ it has reversed its direction in the laboratory coordinate system. The spectrum of an ensemble of randomly oriented nonrotating molecules would consist of two sharp peaks with separation $3A$. In liquid, the separation is A or one-third the apparently isotropic splitting of the nonrotating molecules. The phenomenon occurs because at sufficiently rapid molecular reorientation the nuclear spins do not follow adiabatically the reorientation of the local field; they remain fixed in the laboratory frame. The contribution of the traceless part of the interaction vanishes when it is computed for states in which the spin orientations remain fixed in the laboratory frame.

Another example of the same sort of phenomena is observed at zero field. In the radical ion $(SO_3)_2NO^{=}$, whose hyperfine tensor is similar to those of the nitroxide spin labels, the observed zero-field spectrum in fluid media is accurately accounted for by only the isotropic part of the tensor.[10] As the molecule tumbles rapidly in zero field its spin angular momentum retains its orientation in the laboratory frame.

Finally we discuss one other phenomenon—migration of triplet excitation energy—which has analogies to the reorientation phenomena. The first instance was discovered by van der Waals and de Groot in their studies of the triplet esr spectra of tribenzotriptycene, a molecule with three naphthalene-like pieces arranged in trigonal symmetry. They found that at 4 K the esr spectrum resembled that of naphthalene but that at 77 K the spectrum had collapsed to a narrower one characteristic of a molecule with trigonal symmetry.[11] They interpreted the observation as resulting from a temperature-dependent stochastic hopping of triplet excitation among the three rings. A simpler case has recently been described by Shain in his study of a series of spiro compounds containing two fluorene-like groups perpendicular to each other.[12] He supposed that the triplet excitation jumps between the two aromatic groups and calculated the spectral shapes as a function of jumping rate in a manner completely analogous to those used for reorienting molecules. The jump of triplet excitation between the two noncoplanar aromatic systems

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(10) J. Townsend, S. Weissman, and G. Pake, *Phys. Rev.*, **89**, 606 (1953).

(11) M. de Groot and J. van der Waals, *Mol. Phys.*, **6**, 545 (1963).

(12) A. Shain, *J. Chem. Phys.*, **56**, 6201 (1972).

is treated as if the single aromatic system containing triplet excitation suddenly jumps to the orientation of the system which receives the excitation. Although his interpretation probably does not include important components of the phenomenon, it yields a remarkably satisfactory account of the temperature dependence of the spectra.

The work here reported has been supported by the National Science Foundation and by the Petroleum Research Fund, administered by the American Chemical Society.

Ab Initio Studies of Molecules and Concepts of Molecular Structure

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Received October 2, 1972

For more than a decade much effort has been devoted to the construction of electronic wave functions by so-called *ab initio* techniques with the hope that the predictive capabilities of quantum mechanics could be realized for atoms and molecules.

For this purpose, wave functions and energies usually are determined by energy-variational calculations since the Schrödinger equation is not amenable to direct solution. Conventionally self-consistent-field (SCF) or configuration interaction (CI) formulations have provided the main routes toward approximate solutions. The single-determinant of orbitals form of the total wave function, which is most frequently used in SCF theory, cannot in principle lead to an exact solution, while a CI construction can in principle, but only in the unattainable limit of a complete basis set. Thus, at the levels applied in practice, both methods are imperfect formulations of the many-electron problem. The terminology *ab initio,* as generally used, thus has become associated with the fact that interactions, usually in the form of integrals, are evaluated accurately. It does not mean that the form of the wave function itself is not unduly constrained.

This Account examines some of the main ideas of many-electron theory, discusses some of the successes of computations and some of the uncertainties and failures, and hopefully provides some insight into how some of the *ab initio* conclusions can be incorporated into qualitative lines of reasoning.[1]

Many-Electron Orbital Theory Assumptions

If the dynamics of nuclear motion is not of interest, the nuclei can be considered fixed in space at some chosen geometry which can later be varied (Born–Oppenheimer approximation), giving the Hamiltonian

$$H = \underbrace{\sum_{i}^{N} -\tfrac{1}{2}\nabla_i^2}_{\text{el kinetic energy}} + \underbrace{\sum_{i}^{N}\sum_{k}^{M} -\frac{Z_k}{r_{ik}}}_{\text{el–nuc attraction}} + \underbrace{\sum_{i<j}^{N}\frac{1}{r_{ij}}}_{\text{el–el repulsion}} + \underbrace{\sum_{k<l}^{M}\frac{Z_kZ_l}{R_{kl}}}_{\text{nuc–nuc repulsion}} + \underbrace{H'}_{\text{other interactions}}$$

where i and j label the N electrons and k and l label the M nuclei. Contributions, H', due to magnetic interactions or external fields, if sufficiently small, can be neglected in determining the electronic structure, and this assumption is made here. The problem is to solve the Schrödinger equation, $H\Psi_k = E\Psi_k$, for the antisymmetric state functions. For many-electron systems, a direct attack on the differential equation has not led to sufficiently accurate approximations.

This difficulty can be resolved by translating the problem into an equally valid integral form, the energy-variational principle, $E_{\text{exact}} \leq E = \langle\Psi|H|\Psi\rangle$, for ground states, and under known conditions for excited states as well. Wave functions and energies can now be determined by minimizing the average value of the energy of the system with respect to variations of Ψ. The orbital approach has been the most fruitful, both to determine the simplest approximation and to establish a starting point for refinements of Ψ. Its origins can be traced to a crucial approximation, that of replacing the real electron–electron potential by an effective independent particle potential. If this is done, the exact solutions of the modified problem can be expressed either as a simple product of spin orbitals or as a single Slater determinant,[2] $\Psi = \det(\chi_1(1)\chi_2(2)\ \ldots\ \chi_N(N))$, the latter

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(1) A recent survey of *ab initio* quantum mechanical calculations is contained in H. F. Schaefer, III, "The Electronic Structure of Atoms and Molecules," Addison-Wesley, Reading, Mass., 1972.

(2) J. C. Slater, *Phys. Rev.*, **34,** 1293 (1929); **36,** 57 (1930).