Either representation may be employed. Notice that for the validity of this formalism σ must be parametrized. The generating functional for any u.t. must satisfy the integrability conditions.

The Heisenberg representation for any field theory may formally be set up by taking everything over unchanged from classical dynamics. It is readily verified in simple cases that no inconsistency arises. The interaction representation may be constructed with the help of the general theorem, that any c.t. generated by an infinitesimal c.t. may always be performed before transition from classical to quantum mechanics.

Divide the classical $\mathcal{H}$ and $\mathfrak{h}_r$ into two parts, $\mathcal{H}=\mathcal{H}^f+\mathcal{H}^i$, $\mathfrak{h}_r=\mathfrak{h}_r{}^f+\mathfrak{h}_r{}^i$, $\mathcal{H}^f$ and $\mathfrak{h}^f$ being derived from the "free" Lagrangian $\mathcal{L}^f$. Then each part will satisfy Eq. (2) of I. New variables $\varphi^{*\alpha}(\sigma, \tau)$, $\pi_\alpha{}^*(\sigma, \tau)$ depending on two surfaces are introduced by the c.t. $(\delta W/\delta w)+\mathcal{H}^f=0$, $(\delta W/\delta u^r)+\mathfrak{h}_r{}^f=0$ for variations of τ. They satisfy canonical equations with H^i, $h_r{}^i$ for variations of σ, and are equal to the original variables when $\sigma=\tau$. This is identical with classical perturbation theory.

With the aid of a one-parameter family of surfaces τ: $x^\mu=f^\mu(\rho, u^1, u^2, u^3)$ with σ as one member, one may introduce field variables $\varphi^{*\alpha}(\sigma, x)$ related to $\varphi^{*\alpha}(\sigma, \tau)$ and $\pi_\alpha{}^*(\sigma, \tau)$ by a transformation depending on τ. These depend on both a point and a surface σ and satisfy "free" field equations and P. B. relations.

Now use the Heisenberg representation for variations of τ and the Schrödinger representation for variations of σ. Then the operators vary only with τ and the wave functional only with σ, according to Eq. (2) with $\mathcal{H}^f$, $\mathfrak{h}_r{}^f$ and Eq. (4) with $\mathcal{H}^i$, $\mathfrak{h}_r{}^i$. *It is most important to notice that these equations refer to parametrized surfaces.* In particular the variation of Ψ is determined relative to a basis formed by the eigenvectors of a complete commuting set of variables constant under all transformations of τ.

But it is more usual to employ a representation whose basis is defined by a complete set of commuting functions of the field variables which commute with $P_0{}^f$. The two are not the same: The field quantities are related to the canonical variables by a transformation which depends on the particular set of surfaces τ. In the new representation the surfaces are no longer parametrized, and a solution of the Schrödinger equation is

$$\Psi[\sigma_1]=\Phi[\sigma_0]+\left(\frac{1}{i\hbar}\right)\int_{\sigma_0}^{\sigma_1}\mathcal{L}^i(x)\Psi[\sigma]dx, \tag{5}$$

where $\mathcal{L}^i$ is the interaction Lagrangian. The S matrix is

$$\sum_{n=0}^{\infty}\left(\frac{1}{i\hbar}\right)^n\frac{1}{n!}\int_{-\infty}^{\infty}dx^{(1)}\cdots\int_{-\infty}^{\infty}dx^{(n)}P[\mathcal{L}^i(x^{(1)})\cdots\mathcal{L}^i(x^{(n)})]. \tag{6}$$

Expressions equivalent to (6) have been found in particular cases by Belinfante[3] and Matthews.[4] The results of I and this paper will be discussed in detail elsewhere.

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Determination of g-Values in Paramagnetic Organic Compounds by Microwave Resonance

A. N. Holden, C. Kittel, F. R. Merritt, and W. A. Yager
Bell Telephone Laboratories, Murray Hill, New Jersey

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Microwave magnetic resonance absorption was observed near 24,000 mc/sec. at room temperature in three organic free radical compounds, and accurate determinations of the g-values in the resonance equation $\hbar\omega=g\mu_BH$ were made by comparison with the proton resonance frequency in the same magnetic field. Preliminary results on one of the compounds were reported in an earlier communication.[1] Measurements at 50 and 450 mc/sec. on another free radical, pentaphenyl cyclopentadienyl, have been reported by Kosirev and Salekov.[2] The results of our measurements on polycrystalline specimens are summarized below.

(a) Diphenyl-trinitro phenyl hydrazyl: $(C_6H_5)_2N-NC_6H_2(NO_2)_3$.

The g-value is 2.0036±0.0002, and the half-width of the resonance line at half-power is 1.35 oersteds, which appears to be the sharpest line yet reported for electronic spin resonance. It is possible that the substance may be useful for magnetic field calibration and stabilization. The g-value determination was repeated a large number of times under various experimental conditions; the standard error of the observations is actually less than 1 part in 20,000. Approximate agreement with our g-value is reported independently by Townes and Turkevich.[3] The g-value was calculated by comparing the observed ratio of (proton frequency/electron frequency) with the value

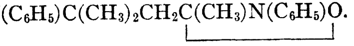
$$\omega_p/\omega_e=(1.51927\pm0.00008)\times10^{-3}$$

for the frequency ratio given by Taub and Kusch,[4] which we take to correspond to the theoretical g-value for electron spin, $g_s=2(1+\alpha/2\pi)=2.0023$, where vacuum polarization and radiation interaction effects are included.

(b) Di-para-anisyl-nitric oxide: $(p-CH_3OC_6H_4)_2NO$.

The g-value is 2.0063±0.0005, and the half-width at half-power is 15.7 oersteds. Crystalline material in which approximately one part of this compound was diluted with ten parts of the isomorphous non-magnetic compound p,p'-dimethoxy benzophenone gave a half-width of 29.6 oersteds. The increase in line width on dilution suggests that the original line was sharpened by exchange narrowing. In both cases the line was quite flat on top which suggested a hyperfine splitting of about 45 mc/sec. over-all; however, measurements in liquid solution gave a sharper (7 oersteds) and well-rounded single line. The flat top in the solid may have been caused by anisotropy of packing of the individual crystallites.

(c) β-(phenyl nitrogen oxide)-β-methyl pentane-δ-one oxime N-phenyl ether:



$ON(C_6H_5)C(CH_3)_2CH_2\underline{C(CH_3)N(C_6H_5)O}$.

The g-value is 2.0057±0.0002, and the half-width at half-power is 9.2 oersteds. The larger width we reported previously[1] was caused in part by magnet overheating. Single crystals of this substance have been grown and some measurements made. As expected, the g-value is quite anisotropic, ranging between 2.0035 and 2.0073 in different orientations. This compound was also measured in benzene solution: the resonance was rather weak and broad, with no observable hyperfine splitting.

The half-widths calculated for the above compounds on the basis of dipole-dipole interactions alone are of the order of 100 oersteds. The observed widths are between 6 and 70 times sharper, even in polycrystalline specimens, and the effect may be ascribed to the Gorter-Van Vleck process of exchange narrowing. The existence of significant exchange forces is supported in the case of compound (a) above by magnetic susceptibility measurements,[5, 6] which give an antiferromagnetic θ in the Curie law of 10°K to 20°K; and in compound (b) the antiferromagnetic θ is 13°K.

The deviations of the g-values from the spin-only value of 2.0023 are 0.0013, 0.0040, 0.0034, in compounds (a), (b), (c), respectively. The excess is presumably to be ascribed to spin-orbit coupling[7] of the "odd" electron, and the sign of the deviation suggests that the odd electron may be partly localized in a more than half-filled shell, perhaps the $2p$ shell of an oxygen, nitrogen, or carbon atom.

We have employed a super-regenerative circuit for detecting proton resonance, and have found that it is possible in some cases for significant errors to arise with this method, as revealed by a dependence of the apparent g-value on the quench frequency of the oscillator. In the worst case, using paraffin wax at 80 kc/sec. quench frequency, the errors in g were of the order of 0.1 percent. In other materials, such as mineral oil, glycerine, and triethanolamine, the objectionable effect did not occur.

We wish to thank J. K. Galt for assistance in setting up the proton resonance equipment, and S. Millman for several valuable discussions.

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Hyperfine Structure and Exchange Narrowing of Paramagnetic Resonance†

C. H. TOWNES* AND J. TURKEVICH**
Brookhaven National Laboratory, Upton, Long Island, New York
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THE free radical α, α-diphenyl β-picryl hydrazyl, $(C_6H_5)_2N-NC_6H_2(NO_2)_3$, shows the strongest and narrowest electronic paramagnetic resonance absorption so far reported. This resonance was observed by its effect on the transmission of microwaves (frequency approximately 24,000 mc) through a TE_{01} cavity with a small amount of the free radical placed approximately on the axis of the cavity. The microwave frequency was tuned to give maximum transmission through the cavity while the cavity was in place between the pole pieces of an electromagnet. With an amount of the free radical as small as 2 mg the transmitted power was reduced by a factor of three when the magnetic field was of the proper value (approximately 8600 oersteds) to give resonance. The half-width of the resonance at half-maximum absorption was 1.45 oersteds. Because of its sharpness and intensity, this resonance may be of value for stabilizing or measuring magnetic fields in cases where the signal produced by the proton resonance is not sufficiently strong.

The electronic g-value was obtained by measuring the electron's resonant frequency and the proton frequency in the same magnetic field. The ratio of proton to electron frequencies obtained was 15.178×10^{-4} which, combined with results of Taub and Kusch,[1] gives a g-value of 2.0042 ± 0.0004. The g-value and line width obtained are in fair agreement with the results of Holden, Kittel, Merritt, and Yager,[2] who have made measurements parallel to those presented here and with whom we have enjoyed very helpful discussions.

The unusually narrow line-width observed is evidently due to exchange narrowing[3] since spin-spin interactions alone would lead one to expect a half-width of approximately 50 oersteds. The free radical was dissolved in concentrations of 3.0 and 1.5 weight percent in benzene and the resonance width examined. With these dilutions exchange effects should be negligible, and indeed the resonance half-widths (half-widths at half-maximum) were greater than in the solid, being 7.5 and 5 oersteds respectively for the two solutions. These latter widths are, as closely as can be calculated, just those to be expected from spin-spin interactions. Motion of the molecules in solution gives no appreciable narrowing of the line at the frequencies used since the relaxation time is 10^{-10} sec. or larger.

Gaseous NO has been examined by Beringer and Castle[4] with a somewhat similar technique. They find associated with the electronic resonance a hyperfine structure due to coupling between the N^{14} and electronic magnetic moments. If the odd electron in NO is considered to be on the nitrogen atom in an essentially atomic $2p$ state, the expected interaction is approximately 75 $I\cdot J$ megacycles/sec. Here the average inverse cube of the electron's distance from the nucleus has been taken from a previous estimate for nuclear quadrupole effects.[5] The experimental results give an interaction of 31 $I\cdot J$ mc, indicating that the probability of finding the odd electron on the nitrogen atom is approximately $\frac{1}{2}$. This is what may be expected if the electron participates in a 3-electron bond.[6]

The free radical examined here is in a $^2\Sigma$ electronic state and the odd electron might be assumed to be in a $2p$ orbit on the nitrogen atom which has only two bonds. In this case hyperfine structure consisting of three equally spaced, equal intensity lines separated by 125 mc or 45 gauss may be expected. If exchange interactions between the electrons in adjacent molecules are as large as the electron-nuclear coupling, this hyperfine structure may be considerably modified or eliminated. Since the exchange effects are evidently important in the solid material, failure to find hyperfine structure is perhaps not surprising. However, in the diluted solutions of the free radical hyperfine structure of the type described was expected, but not found. What hyperfine splitting is present must be less than the line width, hence the probability of finding the odd electron on the nitrogen which formerly has only two valence bonds must be less than 0.15. In order to produce such a small hyperfine structure, this electron must either have considerable probability of being found on nuclei of zero spin such as oxygen, or perhaps circulate over a considerable region of the molecule and hence average out a large number of small interactions with nuclei.

Study of hyperfine structure in other molecules with magnetic moments of electronic origin should give considerable information about the electron distributions.

The interest and encouragement of Dr. W. V. Cohen during this investigation is appreciated. In addition we are indebted to Mr. Walter Merkle for making available the Brookhaven cyclotron magnet in which this work was carried out, and to Mr. George Brush and others of the cyclotron group for considerable assistance.

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* Permanent address: Columbia University, New York, New York.
** Permanent address: Princeton University, Princeton, New Jersey.
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Microwave Spectrum of CH_2CFCl

J. K. BRAGG, T. C. MADISON, AND A. H. SHARBAUGH
Research Laboratory, General Electric Company, Schenectady, New York
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THE microwave spectrum of the asymmetric top molecule CH_2CFCl has been observed and analyzed. The molecular parameters for both isotopic species are given in Table I. The frequencies computed with these parameters for the transitions which have been identified appear in Table II, together with the observed frequencies corrected for quadrupole effect.

The assignments of these lines were further confirmed, in every case, by the agreement (0.5 percent) of the observed quadrupole multiplet structure with that computed by first-order theory.[1] The quadrupole parameters used were $\chi_{aa}=-73.3\pm0.3$ megacycle/second and $\chi_{bb}=39.8\pm0.2$ megacycle/second. The quan-

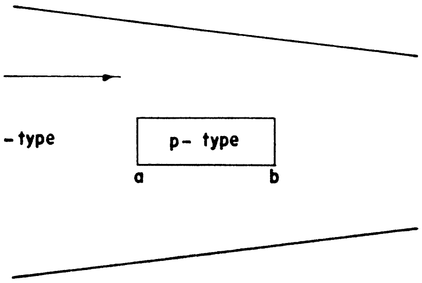

FIG. 1. $6_{24}\rightarrow6_{33}$ multiplet of CH_2CFCl.