the factor

$$\frac{\omega+\omega_e}{\omega-\omega_e}-\frac{k_{\|}^2 v_A^2}{2\omega^2}$$

has an extreme value.

Then we obtain a possible maximum width of the potential well

$$\Delta x \approx \frac{1}{8}\left(\frac{L_s}{r}\right)^2\frac{a^2}{r}.$$

If $\Delta x<\lambda_x\approx a\sqrt{r/\Delta x}$, that is, $\Delta x<a^{2/3}r^{1/3}$, the unstable localized solution cannot exist. Then we have a stability criterion

$$L_s/r<2\sqrt{2}\,(r/a)^{2/3}. \qquad \text{(A.39)}$$

Mikhailovskaya and Mikhailovskii [1] also obtained another stability criterion

$$L_s/r<(r/a)^{1/2}\beta^{-1/4}. \qquad \text{(A.40)}$$

Beyond the turning point $x=x_A$, the localized solution is expressed by use of the Airely function [16]

$$\varphi(x)\sim\left(\frac{a^2}{U'(x_A)}\right)^{1/4}(x_A-x)^{-1/4} \times\exp\left\{-\frac{2}{3}\left(\frac{U'(x_A)}{a^2}\right)^{1/2}(x_A-x)^{3/2}\right\}, \qquad \text{(A.41)}$$

where $U'(x_A)$ is roughly given by $\Delta x/r\,x_A$, that is,

$$U'(x_A)\sim\frac{1}{8}\frac{L_s\,a}{r^3\sqrt{\beta}}.$$

Then the characteristic length of exponential decay which we denote by δx is given by

$$\delta x\sim 2\,(a\,r^3\sqrt{\beta}/L_s)^{1/3}.$$

Finally, we can derive the stability criterion Eq. (A.40) from the condition $\delta x>x_A-x_e$ where x_e is defined by $\omega_e\approx k_{\|}v_e$.

Galeev [2] also obtained almost the same criterion as Eq. (A.40). He mentioned that if the transparency condition of a hill between x_A and x_e is satisfied, that is, if

$$\int_{x_e}^{x_A}\sqrt{U(x)}\,dx<1, \qquad \text{(A.42)}$$

the region of existence of the localized solution expands into the ion Landau damping region. The transparency condition Eq. (A.42) is essentially the same as $\delta x>x_A-x_e$. However, his statement is not right because the ion Landau damping region does not lie in a region

$$x<x_e\,(<x_A),$$

but in a region

$$x\sim x_i\gg x_A$$

where x_i is defined $|k_{\|}v_i|=\omega_e$. Eq. (A.40) means that the localized region of the perturbation extends into the region of the electron Landau damping.

[16] H. A. Kramers, Z. Physik **39**, 828 [1926].

A General Formulation for the Evaluation of Two-center Moment Integral – An Extension

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(Z. Naturforschg. **22 a**, 1701—1704 [1967]; received 27 June 1967)

In two recent studies [1, 2] we presented a general formulation for the evaluation of two-center moment integrals as well as the rotational properties of s, p, and d atomic orbitals needed in the quantum mechanical calculations of one-electron properties. In the present investigation, we extend the scope of our previous formulation by presenting a series of tabulations useful both to inorganic and organic chemists.

(a) One- and Two-center Transition Moment Integrals

Our most recent investigation of the intensities in the spectrum of XeF_4 (l. c. [3]) has revealed certain useful internal relationships existant in one- and two-center transition moments. These are conveniently reported in Tables 1 and 2. It should be noticed that, in the case of the two-center integrals,

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[1] W. A. Yeranos, Z. Naturforschg. **21 a**, 1864 [1966].
[2] W. A. Yeranos, Inorg. Chem. **5**, 2070 [1966].
[3] W. A. Yeranos, unpublished results.

	$\langle s\,\vert^{0}$	$\langle d_{xy}\vert^{2}$	$\langle d_{yz}\vert^{1}$	$\langle d_{z^2}\vert^{0}$	$\langle d_{xz}\vert^{-1}$	$\langle d_{x^2-y^2}\vert^{-2}$	
X		A					$\vert P_y\rangle^{1}$
Y	D			−B		−A	
Z			A				
X					A		$\vert P_z\rangle^{0}$
Y			A				
Z	D			C			
X	D			−B		A	$\vert P_x\rangle^{-1}$
Y		A					
Z					A		

$B = A/\sqrt{3}$
$C = 2B$

Table 1. One-center transition moment integrals.

	s^{0}	p_y^{1}	p_z^{0}	p_x^{-1}	d_{xy}^{2}	d_{yz}^{1}	$d_{z^2}^{0}$	d_{xz}^{-1}	$d_{x^2-y^2}^{-2}$	
X				W				U		0
Y		W				U				σ
Z	R		M				V			
X					S					1
Y	P		L				T		−S	π_y
Z		L				k				
X	P		L				T		S	-1
Y					S					π_x
Z				L				k		

Table 2. Two-center transition moment integrals.

the bra functions are defined in a right-handed coordinate system, while the ket functions are defined in a left-handed coordinate system. Obviously, if both functions are defined in right-handed coordinate systems, M_2 as defined in our original paper [1] becomes

$$M_2' = (-1)^{l+m} M_2 ,$$

while if both are defined in left-handed coordinate systems, it becomes

$$M_2'' = (-1)^{l'+m'} M_2 .$$

(b) Rotational Transformations of f *Orbitals for the Evaluation of Two-center Integrals*

In a recent note we commented on the rotational transformations of s, p, and d orbitals necessary for the evaluation of two-center integrals [2]. In the present note we extend our previous formulation to the f orbitals. It should be noted that although the f orbitals do not play as important a role in bonding as do the d orbitals, they do, nonetheless, account for the subtle aspects of the chemistry of the elements with atomic numbers 51 to 70 and 83 to 102. The 5f orbitals, for instance, are believed to be responsible for the stability of MO_2^{++} and MO_2^{+} ions [4] of some of the actinides (M = U, Np or Pu), while the 4f orbitals, it has been suggested [5–8], even contribute to the stability of the compounds of a few elements *lighter* than the lanthanides.

Thus, we define ξ, η, α, β, and γ precisely in the same manner as in our previous note [2], and if for ease of writing we set

$$f_{A_0} \equiv f_{x_0(x_0^2-3y_0^2)} ,$$
$$f_{B_0} \equiv f_{z_0(x_0^2-y_0^2)} ,$$
$$f_{C_0} \equiv f_{x_0(5z_0^2-r_0^2)} \sim f_{x_0 z_0^2} ,$$
$$f_{D_0} \equiv f_{z_0(5z_0^2-3r_0^2)} \sim f_{z_0^3} ,$$
$$f_{E_0} \equiv f_{y_0(5z_0^2-r_0^2)} \sim f_{y_0 z_0^2} ,$$
$$f_{F_0} \equiv f_{x_0 y_0 z_0} ,$$
$$f_{G_0} \equiv f_{y_0(3x_0^2-y_0^2)}$$

then for the f orbitals [9, 10] we have

$$\begin{aligned} f_{x(x^2-3y^2)} = {} & \{\xi^6 \cos(3\alpha+3\gamma) - \eta^6 \cos(3\alpha-3\gamma)\} f_{A_0} + \{\sqrt{6}[\xi^5 \eta \cos(2\alpha+3\gamma) + \xi \eta^5 \cos(2\alpha-3\gamma)]\} f_{B_0} \\ & + \{\sqrt{15}[\xi^4 \eta^2 \cos(\alpha+3\gamma) - \xi^2 \eta^4 \cos(\alpha-3\gamma)]\} f_{C_0} + \{2\sqrt{10}\, \xi^3 \eta^3 \cos 3\gamma\} f_{D_0} \\ & + \{\sqrt{15}[\xi^4 \eta^2 \sin(\alpha+3\gamma) - \xi^2 \eta^4 \sin(\alpha-3\gamma)]\} f_{E_0} \\ & + \{\sqrt{6}[\xi^5 \eta \sin(2\alpha+3\gamma) + \xi \eta^5 \sin(2\alpha-3\gamma)]\} f_{F_0} \\ & + \{\xi^6 \sin(3\alpha+3\gamma) - \eta^6 \sin(3\alpha-3\gamma)\} f_{G_0} \end{aligned}$$

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[10] Cl. Becker, J. Chem. Educ. **41**, 358 [1964].

$$
\begin{aligned}
f_{z(x^2-y^2)} &= \{-\sqrt{6}[\xi^5\eta\cos(3\alpha+2\gamma)+\xi\eta^5\cos(3\alpha-2\gamma)]\}f_{A_0}+\{(\xi^6-5\xi^4\eta^2)\cos(2\alpha+2\gamma)\\
&+(5\xi^2\eta^4-\eta^6)\cos(2\alpha-2\gamma)\}f_{B_0}+\{\sqrt{10}[(\xi^5\eta-2\xi^3\eta^3)\cos(\alpha+2\gamma)\\
&-(2\xi^3\eta^3-\xi\eta^5)\cos(\alpha-2\gamma)]\}f_{C_0}+\{2\sqrt{15}(\xi^4\eta^2-\xi^2\eta^4)\cos 2\gamma\}f_{D_0}\\
&+\{\sqrt{10}[(\xi\eta^5-2\xi^3\eta^3)\sin(\alpha+2\gamma)-(2\xi^3\eta^3-\xi^5\eta)\sin(\alpha-2\gamma)]\}f_{E_0}\\
&+\{(\xi^6-5\xi^4\eta^2)\sin(2\alpha+2\gamma)+(5\xi^2\eta^4-\eta^6)\sin(2\alpha-2\gamma)\}f_{F_0}\\
&+\{-\sqrt{6}[\xi^5\eta\sin(3\alpha+2\gamma)+\xi\eta^5\sin(3\alpha-2\gamma)]\}f_{G_0}\\
f_{xz^2} &= \{\sqrt{15}[\xi^4\eta^2\cos(3\alpha+\gamma)-\xi^2\eta^4\cos(3\alpha-\gamma)]\}f_{A_0}+\{-\sqrt{10}[(\xi^5\eta-2\xi^3\eta^3)\cos(2\alpha+\gamma)\\
&-(2\xi^3\eta^3-\xi\eta^5)\cos(2\alpha-\gamma)]\}f_{B_0}+\{(\xi^6-8\xi^4\eta^2+6\xi^2\eta^4)\cos(\alpha+\gamma)\\
&-(\eta^6-8\xi^2\eta^4+6\xi^4\eta^2)\cos(\alpha-\gamma)\}f_{C_0}+\{2\sqrt{6}(\xi^5\eta-3\xi^3\eta^3+\xi\eta^5)\cos\gamma\}f_{D_0}\\
&+\{(\xi^6-8\xi^4\eta^2+6\xi^2\eta^4)\sin(\alpha+\gamma)-(\eta^6-8\xi^2\eta^4+6\xi^4\eta^2)\sin(\alpha-\gamma)\}f_{E_0}\\
&+\{-\sqrt{10}[(\xi^5\eta-2\xi^3\eta^3)\sin(2\alpha+\gamma)-(2\xi^3\eta^3-\xi\eta^5)\sin(2\alpha-\gamma)]\}f_{F_0}\\
&+\{\sqrt{15}[\xi^4\eta^2\sin(3\alpha+\gamma)-\xi^2\eta^4\sin(3\alpha-\gamma)]\}f_{G_0}\\
f_{z^3} &= \{-\sqrt{40}\,\xi^3\eta^3\cos 3\alpha\}f_{A_0}+\{\sqrt{60}(\xi^4\eta^2-\xi^2\eta^4)\cos 2\alpha\}f_{B_0}\\
&+\{-\sqrt{24}(\xi^5\eta-3\xi^3\eta^3+\xi\eta^5)\cos\alpha\}f_{C_0}+\{\xi^6-9\xi^4\eta^2+9\xi^2\eta^4-\eta^6\}f_{D_0}\\
&+\{-\sqrt{24}(\xi^5\eta-3\xi^3\eta^3+\xi\eta^5)\sin\alpha\}f_{E_0}+\{\sqrt{60}(\xi^4\eta^2-\xi^2\eta^4)\sin 2\alpha\}f_{F_0}\\
&+\{-\sqrt{40}\,\xi^3\eta^3\sin 3\alpha\}f_{G_0},\\
f_{yz^2} &= \{-\sqrt{15}[\xi^4\eta^2\sin(3\alpha+\gamma)+\xi^2\eta^4\sin(3\alpha-\gamma)]\}f_{A_0}+\{\sqrt{10}[(\xi^5\eta-2\xi^3\eta^3)\sin(2\alpha+\gamma)\\
&+(2\xi^3\eta^3-\xi\eta^5)\sin(2\alpha-\gamma)]\}f_{B_0}+\{-(\xi^6-8\xi^4\eta^2+6\xi^2\eta^4)\sin(\alpha+\gamma)\\
&-(\eta^6-8\xi^2\eta^4+6\xi^4\eta^2)\sin(\alpha-\gamma)]\}f_{C_0}+\{-2\sqrt{6}(\xi^5\eta-3\xi^3\eta^3+\xi\eta^5)\sin\gamma\}f_{D_0}\\
&+\{(\xi^6-8\xi^4\eta^2+6\xi^2\eta^4)\cos(\alpha+\gamma)+(\eta^6-8\xi^2\eta^4+6\xi^4\eta^2)\cos(\alpha-\gamma)\}f_{E_0}\\
&+\{-\sqrt{10}[(\xi^5\eta-2\xi^3\eta^3)\cos(2\alpha+\gamma)+(2\xi^3\eta^3-\xi\eta^5)\cos(2\alpha-\gamma)]\}f_{F_0}\\
&+\{\sqrt{15}[\xi^4\eta^2\cos(3\alpha+\gamma)+\xi^2\eta^4\cos(3\alpha-\gamma)]\}f_{G_0},\\
f_{xyz} &= \{\sqrt{6}[\xi^5\eta\sin(3\alpha+2\gamma)-\xi\eta^5\sin(3\alpha-2\gamma)]\}f_{A_0}+\{-(\xi^6-5\xi^4\eta^2)\sin(2\alpha+2\gamma)\\
&+(5\xi^2\eta^4-\eta^6)\sin(2\alpha-2\gamma)\}f_{B_0}+\{-\sqrt{10}[(\xi^5\eta-2\xi^3\eta^3)\sin(\alpha+2\gamma)\\
&+(2\xi^3\eta^3-\xi\eta^5)\sin(\alpha-2\gamma)]\}f_{C_0}+\{-2\sqrt{15}(\xi^4\eta^2-\xi^2\eta^4)\sin 2\gamma\}f_{D_0}\\
&+\{\sqrt{10}[(\xi^5\eta-2\xi^3\eta^3)\cos(\alpha+2\gamma)+(2\xi^3\eta^3-\xi\eta^5)\cos(\alpha-2\gamma)]\}f_{E_0}\\
&+\{(\xi^6-5\xi^4\eta^2)\cos(2\alpha+2\gamma)-(5\xi^2\eta^4-\eta^6)\cos(2\alpha-2\gamma)\}f_{F_0}\\
&+\{-\sqrt{6}[\xi^5\eta\cos(3\alpha+2\gamma)-\xi\eta^5\cos(3\alpha-2\gamma)]\}f_{G_0},\\
f_{y(3x^2-y^2)} &= \{-\xi^6\sin(3\alpha+3\gamma)-\eta^6\sin(3\alpha-3\gamma)\}f_{A_0}\\
&+\{-\sqrt{6}[\xi^5\eta\sin(2\alpha+3\gamma)-\xi\eta^5\sin(2\alpha-3\gamma)]\}f_{B_0}\\
&+\{-\sqrt{15}]\xi^4\eta^2\sin(\alpha+3\gamma)+\xi^2\eta^4\sin(\alpha-3\gamma)]\}f_{C_0}\\
&+\{-2\sqrt{10}\,\xi^3\eta^3\sin 3\gamma\}f_{D_0}+\{\sqrt{15}[\xi^4\eta^2\cos(\alpha+3\gamma)+\xi^2\eta^4\cos(\alpha-3\gamma)]\}f_{E_0}\\
&+\{\sqrt{6}[\xi^5\eta\cos(2\alpha+3\gamma)-\xi\eta^5\cos(2\alpha-3\gamma)]\}f_{F_0}+\{\xi^6\cos(3\alpha+3\gamma)+\eta^6\cos(3\alpha-3\gamma)\}f_{G_0}.
\end{aligned}
$$

(c) Carbon-Carbon Overlaps and Transition Moment Integrals

In the simple LCAO-MO HÜCKEL formalism, orbitals defined on different centers are assumed to be orthonormal, while, on the other hand, in higher order approximations overlaps between non-adjacent carbon π orbitals are indeed included. It can be shown [11] that the overlap S_{ij} for a pair of homonuclear SLATER $2p_\pi$ AO's x_i and x_j is given by

$$S_{ij}=e^{-\varrho/2}[1+(\varrho/2)+(\varrho^2/10)+(\varrho^3/120)]\,,$$
$$\varrho=Z'\,R/a_0$$

where a_0 is BOHR's radius, Z' the effective nuclear charge (for carbon $Z'=3.25$) and R is the inter-

[11] J. H. BARTLETT, JR., Phys. Rev. **37**, 507 [1931]. – R. S. MULLIKEN, C. A. RIEKE, D. ORLOFF, and H. ORLOFF, J. Chem. Phys. **17**, 1248 [1949].

nuclear distance in Angstroms (Å). The broken curve of Fig. 1 gives the variation of S_{C-C} with the C – C distance ranging from the distance of C≡C in acetylene (1.20 Å) to the one of C – C in ethane (1.54 Å). The solid curves, on the other hand, give the overlaps ($\gamma = 0$) as well as the transition moment integrals ($\gamma = 1$) for a pair of carbon SCF atomic functions given by CLEMENTI [12]. The radial function used for carbon is the ground state's (^{3}P) and is given by

$$R(2p) = 0.5777\,\varphi_2(1.4209) + 0.23561\,\varphi_2(2.5873) + 0.24762\,\varphi_2(0.9554) + 0.01090\,\varphi_2(6.3438)$$

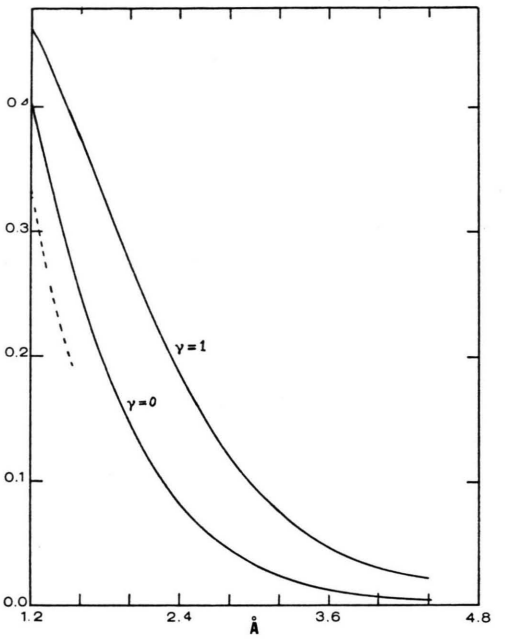

Fig. 1. $\langle \pi' | Z_\gamma | \pi \rangle$ values of carbon as a function of internuclear distance in Å.

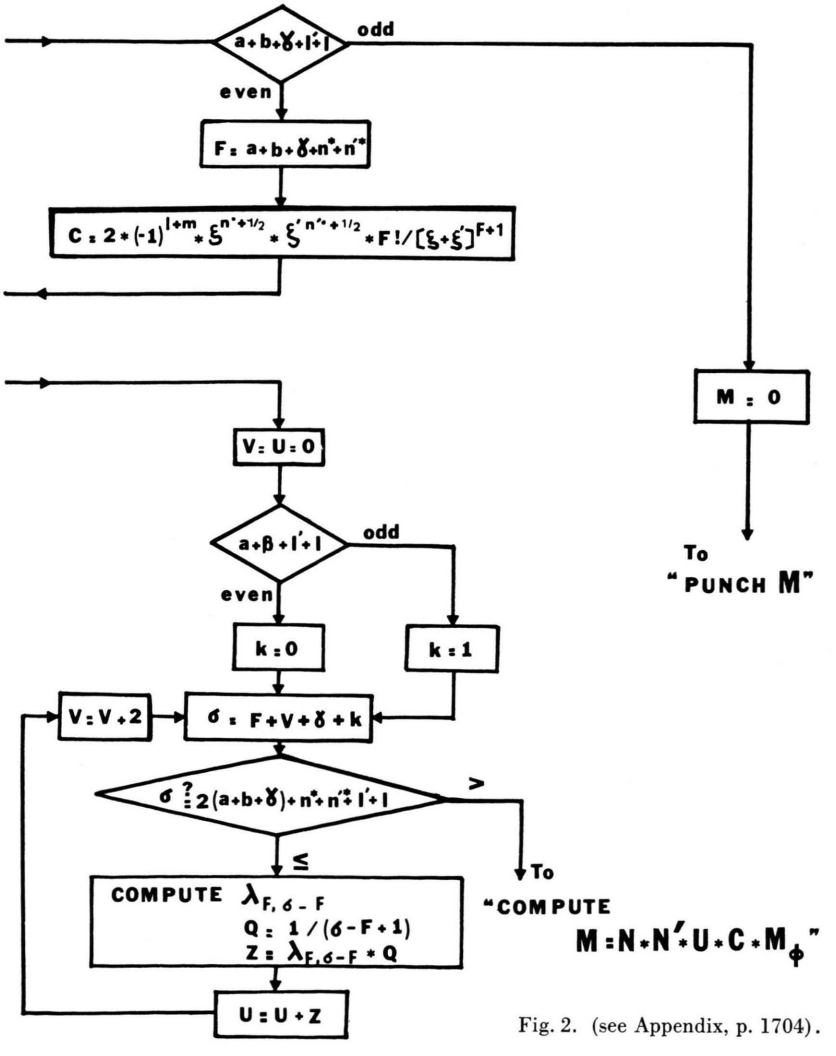

Fig. 2. (see Appendix, p. 1704).

where $\varphi_n(\xi) = N_n r^{n-1} e^{-\xi r}$, N_n being the normalization constant. Table 3, on the other hand, gives the values of these integrals as a function of their internuclear distance.

Distance (Å)	$\gamma = 0$	$\gamma = 1$
1.2	0.4080	0.4628
1.3	0.3618	0.4446
1.4	0.3197	0.4231
1.5	0.2817	0.3994
1.6	0.2475	0.3743
1.7	0.2169	0.3486
1.8	0.1897	0.3228
1.9	0.1656	0.2975
2.0	0.1443	0.2729
2.1	0.1256	0.2493
2.2	0.1091	0.2269
2.3	0.0946	0.2058
2.4	0.0820	0.1861
2.5	0.0710	0.1678
2.6	0.0614	0.1509
2.7	0.0530	0.1355
2.8	0.0458	0.1213
2.9	0.0395	0.1084
3.0	0.0341	0.0967
3.1	0.0293	0.0861
3.2	0.0253	0.0765
3.6	0.0138	0.0472

Appendix

In a recent study [1] we reported a general formulation for the evaluation of two-center moment integrals, and presented therein a computer program for the coding of the said formulation. Unfortunately, however, for some unexplicable reason, the part that dealt with the coding of the one-center integrals, the right-hand side of the flow chart of Fig. 2, seems to be totally erroneous. Consequently, we would like herewith to present the correct version in Fig. 2 (see p. 1703).

[12] E. CLEMENTI, IBM J. Res. Develop. **9**, 2 [1965].

Wie genau kann man heute in der EPR-Spektroskopie g-Faktoren messen?

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In the past few years theoretical aspects of the g-factors of aromatic hydrocarbon radicals have been developed. Since the g-factor variation of these radicals is only of the order of 10^{-4} precise measurements of these quantities are clearly called for. Absolute g-factor measurements are performed according to the equation $g = C\,\omega/\omega_p$. A survey of the different determinations of the conversion factor $C = 2\,\gamma_p'\,m\,c/e$ is given and a value of $C = 3.0419890 \times 10^{-3} \pm 0.5$ ppm is proposed for a well defined proton NMR probe. The most important effects are discussed which may shift the measured EPR and NMR frequencies ω and ω_p.

In der paramagnetischen Elektronenresonanz(EPR)-Spektroskopie der Übergangselemente wird bereits seit geraumer Zeit der g-Faktor der Elektronenhülle theoretisch und experimentell ausführlich untersucht [1]. Im Gegensatz zu den Ionen der Übergangsmetalle liegen bei den aromatischen Kohlenwasserstoff-Radikalen die Variationen des g-Faktors nur in der Größenordnung von 10^{-4} (100 ppm). Zur Untersuchung von Gesetzmäßigkeiten ist also eine beträchtliche Meßgenauigkeit erforderlich. Da es nunmehr – zumindest im Prinzip – möglich geworden ist, die g-Faktoren selbst sehr komplizierter organischer Radikale theoretisch vorherzusagen [2], sind auch vom experimentellen Standpunkt aus diese Größen inter-

[1] Literaturübersicht in: M. BERSOHN u. J. C. BAIRD, An Introduction to Electron Paramagnetic Resonance, W. A. Benjamin, New York 1966.

[2] A. J. STONE, Proc. Roy. Soc. London A **271**, 424 [1963]; Mol. Phys. **6**, 509 [1963]; **7**, 311 [1964].