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Description of the Distribution of Electrons in the Methane Molecule*†

ALMON G. TURNER, ANTONY F. SATURNO, PETER HAUK,‡ AND ROBERT G. PARR§‖
Department of Chemistry, Carnegie Institute of Technology, Pittsburgh, Pennsylvania 15213

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A formal scheme is presented for describing the electron distribution in the methane molecule. Purely theoretical electron density contour maps for the ground state of the molecule are displayed, and various aspects of the electronic distribution are discussed. The electronic wavefunction employed is an analytical form composed of atomic orbitals of *s* through *g* type centered on the carbon nucleus.

The electronic charge density ρ is expressed as a series of normalized (to 4π) tetrahedral harmonics $T_l(\theta,\phi)$, which are certain symmetrical linear combinations of spherical harmonics of the given l value. Namely,

$$4\pi\rho(r,\theta,\phi)=\Sigma_l A_l(r)\,T_l(\theta,\phi),$$

where the $A_l(r)$ depend only on r, the radial distance from the carbon nucleus. The functions $A_l(r)$ are tabulated, and contour maps of ρ are developed. The molecular octupole moment is predicted to be about $1.7\times10^{-34}e\cdot\text{cm}^3$.

The distribution of electrons in a single carbon–hydrogen bond is considered from several points of view, with the purpose, among others, of elucidating the question of the sign and magnitude of the "CH bond moment."

INTRODUCTION

THE shape of a molecule is determined by the distribution of both nuclear and electronic charges within it. Although the nuclear geometry of most molecules is known, where the electrons are is usually only roughly understood. The question of electron locations has always been a focal point in theories of valence; any full understanding of molecular events, including chemical reactions, must be concerned with this.

There is no doubt that accurate quantitative answers to precise questions about electronic motions in simple molecules will soon become available from pure theory, through contemporary advances in methods and techniques for determination of molecular wavefunctions by direct solution of the Schrödinger equation. To be sure, large scale theoretical predictions of properties of molecules of interest to organic chemists are a long way off. But some of the concepts useful in discussions of properties of organic molecules may be critically evaluated in the context of small molecules.

For example, there has been a long-standing discussion concerning the polarity (or lack of it) in a CH bond, and one is beginning to obtain reasonably good wavefunctions for simple molecules and fragments such as CH, CH_2, CH_3, CH_4, and CH_5^+. Perhaps examination of the details of the electron distributions in such species, as given by good wavefunctions for them, could help settle the question of the CH bond moment. Certainly if the wavefunctions are accurate enough definitive answers can be given to any unambiguous question that is asked.

In the present paper, a certain relatively good electronic wavefunction for methane[1,2] is scrutinized for its implications about the charge distribution in this molecule. Contour maps of the electron charge density are displayed and discussed, the electrical moments are calculated, and the electron distribution in the molecule relative to that in the separated atoms is examined. The "CH bond moment" in the molecule also is considered.

CHARGE DENSITY

The density of electrons in a molecule (say in electrons per cm^3) varies with position in the molecule; in methane it may be taken to be a function ρ of the spherical coordinates of a point relative to the carbon nucleus, r, θ, ϕ, or of Cartesian coordinates $X=r\sin\theta\cos\phi$, $Y=r\sin\theta\sin\phi$, $Z=r\cos\theta$. Figure 1 pictures the Cartesian coordinate system chosen.

This density $\rho(r,\theta,\phi)$ is the fraction of the total electronic charge present per unit volume (at r, θ, ϕ), or the probability of finding a unit charge in a unit volume (at r, θ, ϕ) times the total electronic charge. If $\Psi(1,2,\cdots,10)$ is the normalized electronic wavefunction for the system, the density $\rho=\rho(1)=\rho(r,\theta,\phi)$ can thus be determined from the formula

$$\rho=10\int_2\int_3\cdots\int_{10}\Psi^2 d\tau_2 d\tau_3\cdots d\tau_{10}. \qquad (1)$$

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‡ National Science Foundation Predoctoral Fellow, 1958–1962.

§ Alfred P. Sloan Fellow, 1956–1960.

‖ Present addresses: Almon G. Turner, Polytechnic Institute of Brooklyn, Brooklyn, New York; Antony F. Saturno, University of Tennessee, Knoxville, Tennessee; Peter Hauk, California Institute of Technology, Pasadena, California; Robert G. Parr, The Johns Hopkins University, Baltimore, Maryland.

[1] A. F. Saturno and R. G. Parr, J. Chem. Phys. **33**, 22 (1960). In this paper the experimental R_e for methane was carelessly given as 1.093 Å. This is the R_0 value; the correct R_e value is 1.085 Å or 2.05 a_0—see L. S. Bartell, K. Kuchitsu, and R. J. deNeui, J. Chem. Phys. **33**, 1254 (1960).

[2] D. M. Bishop, Mol. Phys. **6**, 305 (1963).

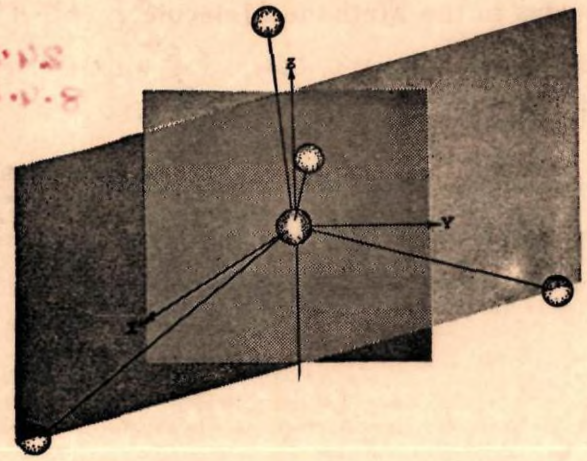

FIG. 1. The methane molecule. In the coordinate system used in the present work, the hydrogen atom at the top of the figure has Cartesian coordinates $X=-S$, $Y=-S$, $Z=+S$, where $S=R/\sqrt{3}$ and $R=2.0\ a_0$; its polar coordinates are R, $\theta=54°44'$, $\phi=225°$. The two planes pictured are the planes for $\phi=-45°$ (the larger plane containing the two lower hydrogen atoms) and $\phi=90°$, respectively.

A final integration gives the total electronic charge,

$$10=\int_1 \rho(1)d\tau_1=\int \rho(r,\theta,\phi)r^2drd\Omega. \qquad (2)$$

In determining ρ from the exact Ψ it makes no difference what coordinates are used, and it makes no difference what mathematical functions are used for describing Ψ; the function ρ as given by Eq. (1) is unique. If only an approximate Ψ is available, the density as computed from Eq. (1) will itself only be approximate.

For the electronic ground state, the charge density ρ must have the full symmetry of the tetrahedral nuclear frame. This means that the function $\rho(r,\theta,\phi)$ if linearly expanded in terms of functions classified by their behavior under the symmetry operations of a regular tetrahedron contains only functions which are unaffected by these symmetry operations. A complete set of such functions in the angular variables θ and ϕ is provided by the totally symmetric *tetrahedral harmonics* $T_l(\theta,\phi)$, the first several of which are listed in Table I. Each of these functions may be compounded from surface harmonics $Y_{lm}(\theta,\phi)$ of the given l value.

TABLE I. The totally symmetric tetrahedral harmonics $T_l(\theta,\phi)$.[a-d]

l	Harmonic
0	1
1	none
2	none
3	$(105)^{\frac{1}{2}}xyz$
4	$(5/4)(21)^{\frac{1}{2}}[x^4+y^4+z^4-(\frac{3}{5})]$
5	none
6	$(231/8)(26)^{\frac{1}{2}}\{x^2y^2z^2+(1/22)[x^4+y^4+z^4-(\frac{3}{5})]-(1/105)\}$
7	$(11/4)(1365)^{\frac{1}{2}}\{xyz[x^4+y^4+z^4-(5/11)]\}$

[a] The harmonics $T_l(\theta,\phi)$ are functions which belong to the totally symmetric representation of the tetrahedral group T_d. Those listed here may be found in D. G. Bell, Rev. Mod. Phys. **26**, 311 (1954).

[b] Here $x=\sin\theta\cos\phi$, $y=\sin\theta\sin\phi$, $z=\cos\theta$.

[c] These functions satisfy the orthonomalization conditions of Eq. (4) of the text.

[d] See Figs. 4 and 5 for graphs of these functions.

TABLE II. The radial distribution functions $A_l(r)$.[a-d]

r	$A_0(r)$	$A_3(r)$	$-A_4(r)$	$A_6(r)$
0.0	∞	0		
0.1	48 0946 600	19	0	
0.2	15 4028 256	559	2	
0.3	5 0691 637	3 454	41	0
0.4	1 8081 392	11 497	290	1
0.5	7959 009	27 415	1 170	7
0.6	4888 672	52 995	3 333	39
0.7	3944 420	88 505	7 464	156
0.8	3581 857	132 495	14 028	471
0.9	3339 494	181 990	23 068	1 144
1.0	3096 466	233 007	34 151	2 336
1.2	2560 004	322 734	58 844	6 571
1.4	2022 192	374 553	79 686	12 467
1.6	1545 769	378 831	90 087	17 705
1.8	1152 684	343 209	88 338	20 134
2.0	842 207	284 259	77 153	19 205
2.2	604 582	218 671	61 223	15 889
2.4	427 432	158 236	44 843	11 689
2.6	298 389	108 839	30 712	7 795
2.8	206 247	71 780	19 879	4 783
3.0	141 515	45 725	12 269	2 733
3.4	65 706	17 125	4 166	748
3.8	30 208	5 945	1 256	169
4.2	13 819	1 964	346	33
4.6	6 300	837	125	9
5.0	2 863	196	21	1
5.4	1 297	60	5	0
5.8	585	18	1	0
6.2	263	5	0	0
6.6	118	2	0	0
7.0	53	0	0	
7.4	23	0		
7.8	10	0		
8.2	5			

[a] See text and Eq. (3) for definition of $A_l(r)$.

[b] Tabulated are values of $A_l(r)\times10^6$ in electrons per a_0^3, calculated as described in Appendix I.

[c] The distance r is in a_0 units. The protons are located at $r=2.0$.

[d] See Figs. 2 and 3 for graphs of these functions.

In terms of them, one may accurately write

$$4\pi\rho(r,\theta,\phi)=\sum_{l=0}^{\infty}A_l(r)T_l(\theta,\phi). \qquad (3)$$

The orthonormalization conditions on the T_l are

$$\int T_l(\theta,\phi)T_{l'}(\theta,\phi)d\Omega=4\pi\delta_{ll'}. \qquad (4)$$

The $l=1$, 2, and 5 terms in the expansion are missing because there are no totally symmetric tetrahedral harmonics for these values of l.

The electronic charge density is completely characterized by the functions $A_l(r)$. The exact wavefunction

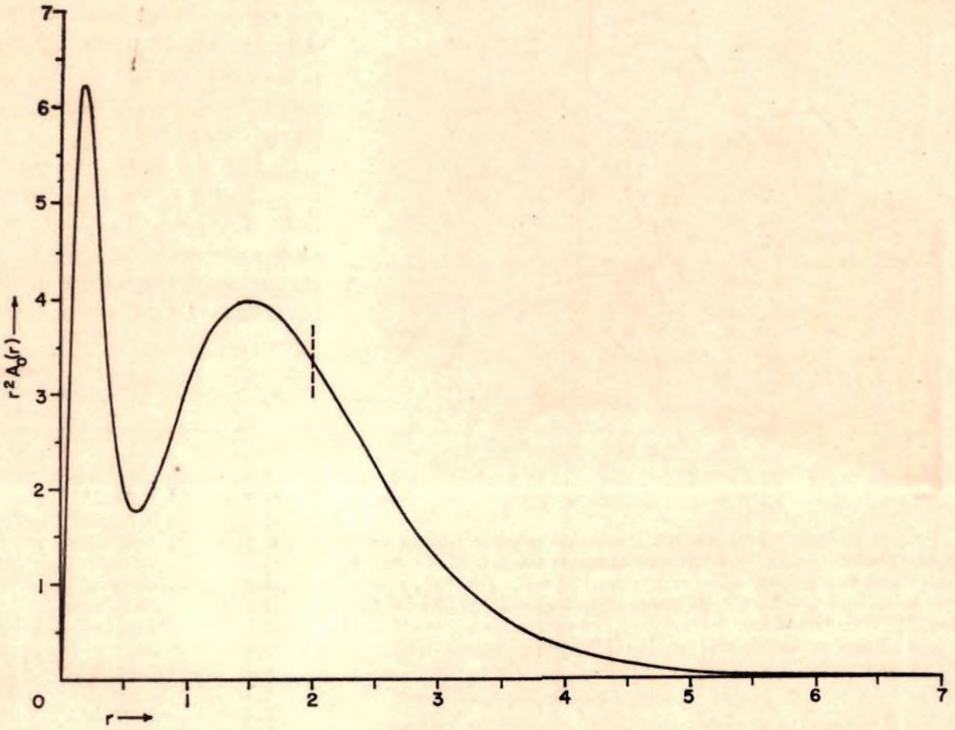

FIG. 2. The spherically symmetrical part of the electron density in methane. Plotted is the radial distribution function $r^2A_0(r)$, where $A_0(r)$ is defined by Eq. (3) of the text. The area under the curve is 10, the total electronic charge. The broken vertical line marks the location of the hydrogen atoms. Atomic units.

defines the exact $A_l(r)$; an approximate wavefunction will give functions $A_l(r)$ differing more or less from the exact.

In Table II are given the functions $A_l(r)$ through $l=6$, as calculated from the wavefunction for methane previously determined in this laboratory. This wavefunction in absolute terms may be described as quite a good one. (See the discussion in Ref. 1.) The functions $A_l(r)$ in Table II should be reasonably close to the true ones, with $A_3(r)$ the least in error and the error increasing with l. Values for $A_7(r)$ are not listed in the table, because significant contributions to A_7 are missing in the wavefunction employed.

The calculation of the $A_l(r)$ from the selected wavefunction is straightforward; details are given in Appendix I.

In Figs. 2–5, the individual $A_l(r)$ and $T_l(\theta, \phi)$ are presented graphically. In Fig. 2 is plotted $r^2A_0(r)$,

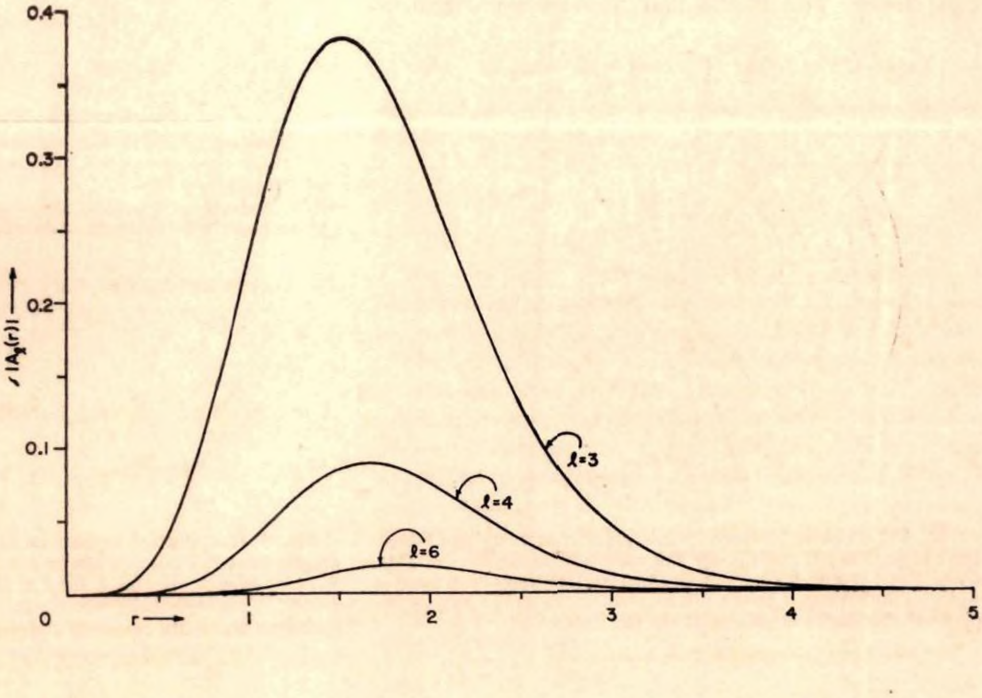

FIG. 3. The radial distribution functions $A_l(r)$ for methane. Plotted are the quantities determining the nonspherically symmetric components of the electron density, as defined in Eq. (3) of the text. $A_3(r)$ and $A_6(r)$ are positive, $A_4(r)$ is negative. Atomic units.

the radial charge density function for the $l=0$ spherically symmetric term. As would be expected, this is a neonlike charge density. The integral under this curve, by Eqs. (2) and (4), is simply the total electronic charge, 10.

In Fig. 3, $A_3(r)$, $A_4(r)$, and $A_6(r)$ are plotted. In Figs. 4 and 5 are illustrated the corresponding functions $T_3(\theta, \phi)$, $T_4(\theta, \phi)$, and $T_6(\theta, \phi)$, for the two planes $\phi=-45°$ and $\phi=90°$ depicted in Fig. 1. These graphs show the nature of the $l>0$ contributions to ρ. Successive terms when superposed upon A_0 concen-

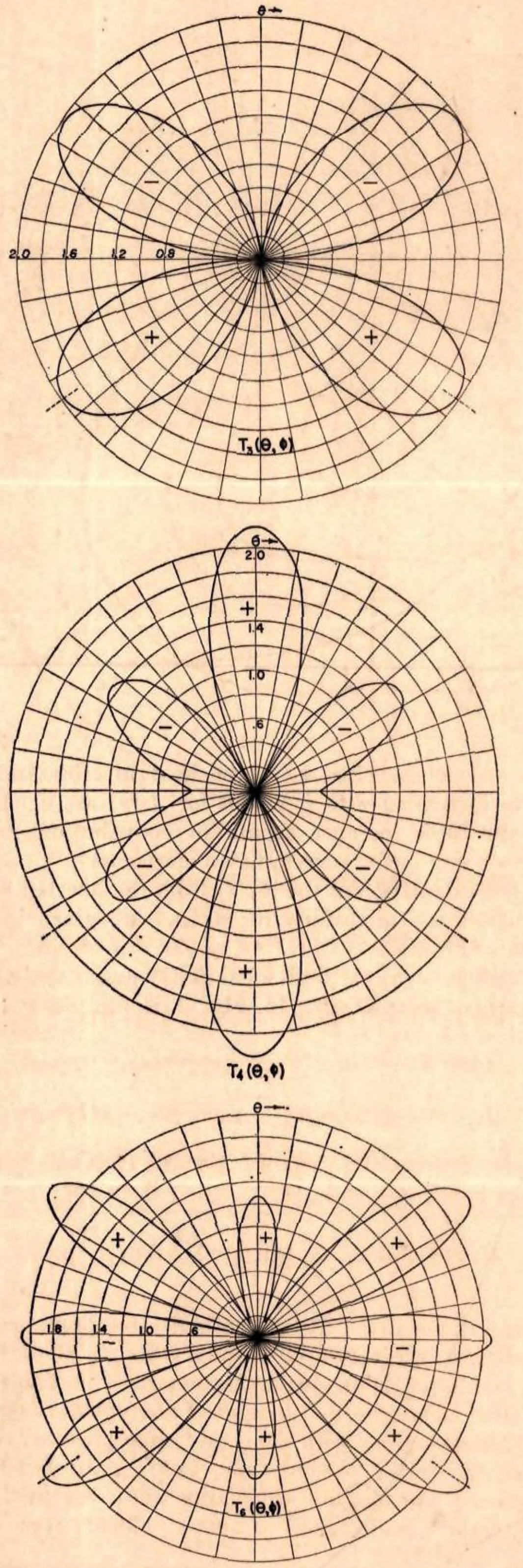

FIG. 4. Tetrahedral harmonics in a plane containing two hydrogen atoms. Plotted radially are the values of the harmonics $T_l(\theta, \phi)$ of Eq. (3) and Table I of the text as functions of θ, for $\phi=-45°$. The hydrogen atoms are located in the lower half of the plane at the angles marked with dotted lines.

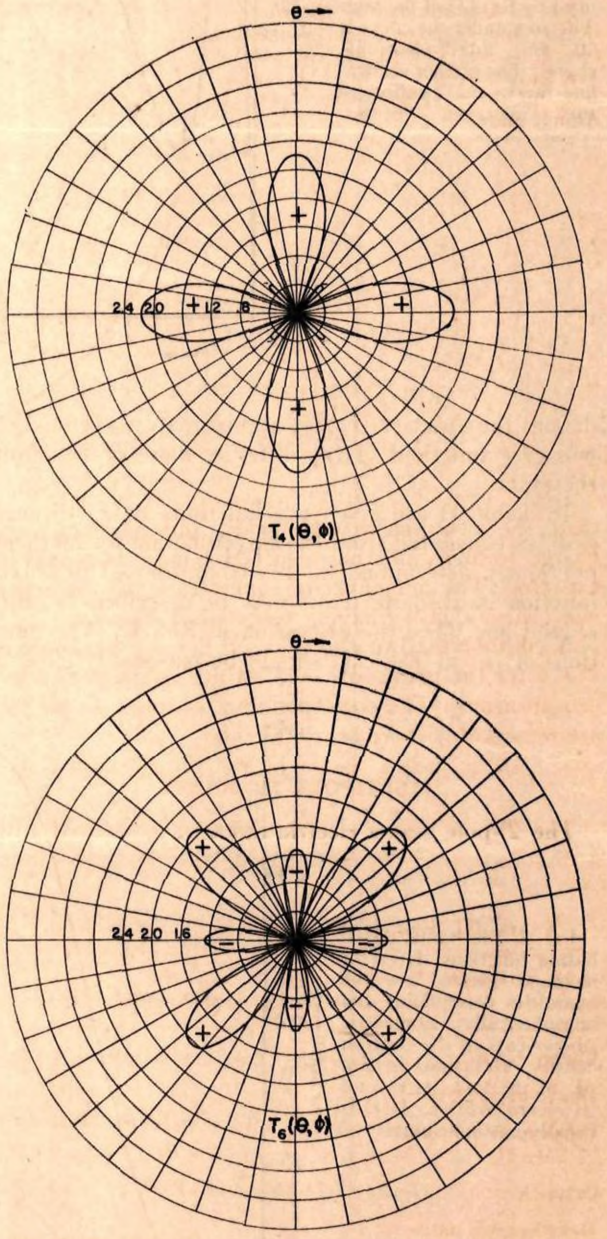

FIG. 5. Tetrahedral harmonics in a plane not containing hydrogen atoms. Plotted radially are the values of the harmonics $T_l(\theta, \phi)$ of Eq. (3) and Table I of the text, as functions of θ, for $\phi=90°$. T_3 is identically zero on the plane, from which all of the hydrogen atoms are equidistant.

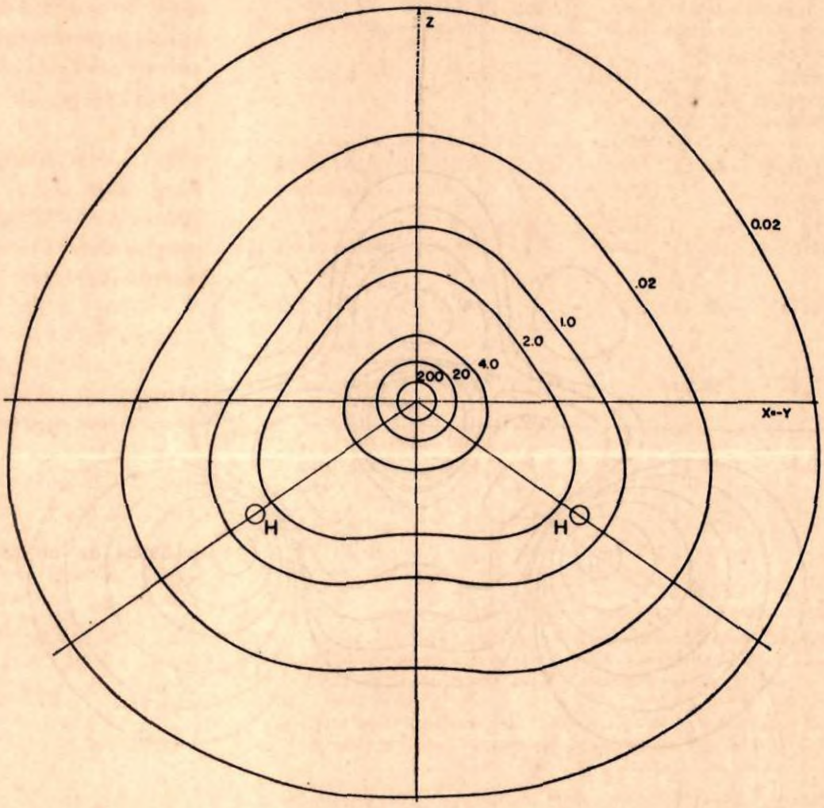

FIG. 6. Contour map of the electron density in methane on a plane containing two H atoms. Plotted are contours of $4\pi\rho$, as calculated from Eq. (A11) of the text, for the $\phi=-45°$ plane of Fig. 1. Atomic units.

trate the electrons in CH bonds, and subtract some charge from regions between CH bonds, as should be expected. The net effect of superposing all the terms is a charge density having tetrahedral shape.

A contour map of the electron density is shown in Fig. 6 for the planes $\phi=-45°$ which contains two hydrogen atoms. The corresponding contours for $\phi=90°$ are remarkably more nearly circular.

MULTIPOLE MOMENTS

The 2^l-pole scalar electric moment associated with a distribution of charge Ω having tetrahedral symmetry may be defined by the formula,[3,4]

$$I_l^{\Omega}=(2l+1)^{-\frac{1}{2}}\int r^l T_l(\theta,\phi)\Omega(r,\theta,\phi)r^2drd\Omega. \quad (5)$$

TABLE III. Electric multipole moments of methane.[a]

Moment[b]	Nuclear contribution[c]	Electronic contribution	Total
Charge ($l=0$)	+10	−10	0
Dipole moment ($l=1$)	0	0	0
Quadrupole moment ($l=2$)	0	0	0
Octupole moment ($l=3$)	+23.85	−11.00	+12.85[d]
Hexadecapole moment ($l=4$)	−36.95	+5.66	−31.29

[a] All values in atomic units: unit of charge e, unit of length a_0.
[b] Moments as defined by Eq. (5) of the text.
[c] From Eq. (6) of text, with $R=2a_0$.
[d] See text for discussion and comparison with experimental values.

For the nuclear frame in methane, this gives[3]

$$I_0^{\text{nuclear}}=+10e, \qquad I_1^{\text{nuclear}}=I_2^{\text{nuclear}}=0,$$
$$I_3^{\text{nuclear}}=\tfrac{2}{3}(20)^{\frac{1}{2}}eR^3, \qquad I_4^{\text{nuclear}}=-4(\tfrac{1}{3})^{\frac{1}{2}}eR^4, \quad (6)$$

where R is the CH distance. For the electrons, on the other hand, one finds, from Eqs. (3) to (5),

$$I_l^{\text{electronic}}=-e(2l+1)^{-\frac{1}{2}}\int_0^\infty r^{l+2}A_l(r)dr. \quad (7)$$

These quantities may be obtained by numerical or analytical integration of the functions $A_l(r)$ of Table II; results of doing this are summarized in Table III.

The theoretically computed octupole moment, $+12.9ea_0^3$, agrees with the best "experimental" value available at the present time, Cole's estimated $9.2-18.5ea_0^3$.[5] The present calculation puts the next moment, the hexadecapole, at about $-30ea_0^4$; apparently

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[3] H. M. James and T. A. Keenan, J. Chem. Phys. **31,** 12 (1959).
[4] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), pp. 839 ff.
[5] D. R. Johnston, G. J. Oudemans, and R. H. Cole, J. Chem. Phys. **33,** 1310 (1960).

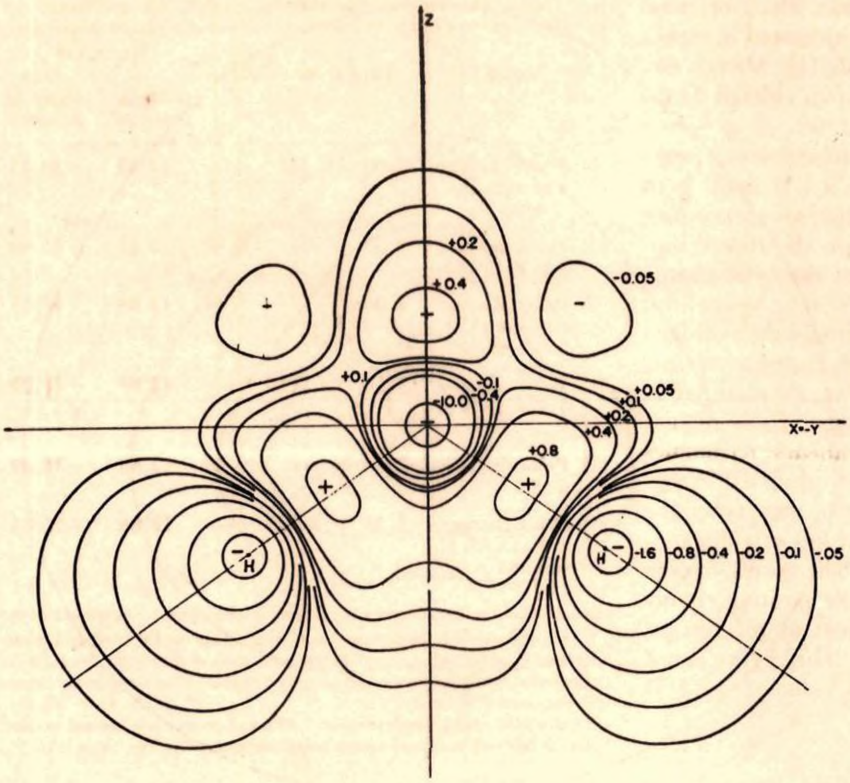

FIG. 7. Contour difference map for methane versus the separated atoms. Plotted are contours of $4\pi[\rho(CH_4) - \rho\ (C+4\ H)]$, determined as described in the text, for the $\phi = -45°$ plane of Fig. 1 that contains two hydrogen atoms. Regions labeled + have a greater electron density in the molecule. Atomic units. For fresh insight, invert.

here is no experimental information bearing on this moment.[6]

CHARGE DENSITY IN THE CH BOND REGION

Figure 6 clearly shows the tetrahedral character of the charge density. It reveals no large concentration of electron density in the CH bond region, however, but rather a general diffuseness. Thus the relative participation in bonding of the hydrogen atoms and the carbon atom is obscured, and from Fig. 6 alone it is not possible to ascertain whether there has been a net transfer of charge from carbon to hydrogen or the reverse.

To answer this question, one might compare the CH_4 electron density with the density that would obtain for a system of four normal hydrogen atoms tetrahedrally located at a distance $2a_0$ from a carbon atom in its $V_4(sxyz)$ valence state. This is done in Fig. 7, which is a difference contour map for the molecule CH_4 versus the atomic system C+4H. The hydrogen densities here merely are densities for $1s$ orbitals on H, charge 1; the carbon density is that associated with an approximate wavefunction of the usual form for the valence state, constructed from Slater orbitals $n_s s$, $n_s s'$, $n_p p$ with $n_s = 0.98619$, $\zeta_s = 5.58706$, $n_s' = 2.08511$ $\zeta_s' = 1.69733$, $n_p = 1.77873$, $\zeta_p = 1.38924$.[7–9]

The implication of Fig. 7 is that in the formation of methane from carbon and hydrogen atoms considerable electronic charge is drawn from the carbon atom into the CH bonds. Charge apparently also is removed from the protons and placed in the bonds. Further, if one visualizes the molecule inscribed in a cube, the four corners not occupied by protons have had a small amount of charge removed from them. There is a slight build up of electron density between adjacent protons, and some extra charge also appears in distant reaches of the molecule.

The foregoing considerations give a qualitative dedescription of the electron distribution in methane and the charge drift that occurs in the formation of methane from the separated atoms, but a quantitative measure of the transfer of charge is still lacking.

To condense the information contained in the electron density maps into a simple quantitative description, one may construct simple one or two parameter electrostatic models for the molecule, which preserve the salient features of its charge distribution. In Table

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[6] One could argue that one should not quote the moments calculated from the best wavefunction for methane in Ref. 2, but one rather should *extrapolate* the results obtained from successively better and better wavefunctions. Moments obtained in this way would be somewhat different.

[7] For the procedure for setting up the valence state wavefunction, see W. Moffitt, Rept. Progr. Phys. **17,** 173 (1954).

[8] These parameters minimize the energy of the valence state wavefunction, giving −37.3408 a.u. for it.

[9] The molecular wavefunction actually employed in the preparation of Figs. 6 and 7 differed very slightly from the wavefunction in Ref. 2.

IV are presented several such models. Each of these models has been chosen to fit the calculated octupole moment of methane as given in Table III; Models (4) and (5) have been made to fit the calculated hexadecapole moment as well.

A somewhat different way of approaching the problem of the distribution of charge in a CH bond is to allocate the nuclear and electronic charges to the four bonds in some way, and to compute the dipole moment of a typical resultant fourth of the total charge distribution. One can do this by dividing space into four equivalent regions, each containing one hydrogen atom. The appropriate quarter-space, called a tetrant, is a three-sided pyramidal section; one is pictured in Fig. 8. After appropriate quadratures, which require the values of certain integrals of tetrahedral harmonics over a tetrant that are discussed and tabulated in Appendix II, one finds that the center of gravity of the $2\frac{1}{2}$ electrons belonging to one tetrant lies at a distance $1.413a_0$ along the CH bond from C. The corresponding center of gravity of one fourth of the positive charge lies at $0.80a_0$. The net over-all moment of the tetrant is $\frac{5}{2}(1.41-0.80)=1.53ea_0=3.89$ D.[10] This figure is not even close to the commonly quoted value of ~0.5 D for the "CH bond moment."

DISCUSSION

It is evident that the concept of the CH bond moment in a molecule such as methane is elusive, illusive, and ill-defined; it should be discussed only in a specified context on a particular operationally defined meaning.

Whether or not there is a pileup of charge right on the protons in CH_4 relative to C+4H is not settled by the present calculations. They indeed do imply a deficiency of electrons at each H, more than compensated by an excess of electrons in the total vicinity of each H. But it is in the very immediate neighborhood of an H that the present method of calculation is worst. And on general grounds one might expect a contraction of the electron cloud about each H due to "cluster promotion".[11] So this point should be investigated further.

Another way to look at the bond moment would be to examine the contributions to the moment of individual equivalent orbitals,[12] obtained from the natural spin orbitals for the molecule by a symmetry transformation to a localized orbital set.[13]

TABLE IV. Simple electrostatic models for methane.

Model	Parameter values[a]			Remarks[b]	
	d	q	μ	octupole moment	hexadecapole moment
(1) Point charges: q at each H, $-4q$ at C	2.00	0.547	...	**12.85**	−20.21
(2) Point dipoles: μ at each H	2.00	...	0.92	**12.85**	−26.60
(3) Point dipoles: μ at each CH bond center	1.00	...	3.65	**12.85**	−13.27
(4) Point charges: q at d, $-4q$ at C	3.14	0.139	...	**12.85**	**−31.29**
(5) Point dipoles: μ at d	2.36	...	0.66	**12.85**	**−31.29**
(6) Point charges: +1 at each H, +4 at C, −2 at d.	1.23	−2.00	...	**12.85**	−26.43

[a] The parameter d is the distance (in a_0 units) along the CH bond axes, measured from C, of four elementary charges q (in units of e) or point dipoles μ (in Debye units). Positive q means net positive charge at d; positive μ means dipole with the sense C^+H^- at d.

[b] Calculated total octupole moment 12.85 a.u., hexadecapole moment −31.29. Values in boldface were used to determine the parameters (See Table III).

Concerning the octupole and hexadecapole moments of methane given in Table III, both of these are probably numerically too large. A careful, though necessarily subjective, consideration of the term-by-term buildup of the quantities that have been calculated in the table suggests that if the calculation of the wavefunction were carried to higher accuracy,[14] the octupole moment would tend to a value near 12 a.u. or $1.7\times10^{-24}e\cdot\text{cm}^3$, and the hexadecapole moment to a value near −25 a.u.

In summary, the most perspicuous description of the charge distribution in methane seems to be provided by comparison of it with the charge distribution in the separated atoms, Fig. 7. As a simple model, Model (6) of Table IV seems best. If one wants to talk about a CH bond moment, one must take care to define the concept. It is notable that 0.5 D quoted for this quantity is not comparable with any number that has been here computed.[15]

APPENDIX I. ANALYSIS OF THE CHARGE DENSITY

The electronic wavefunction selected for methane has the one-center form[1,2]

$$\Psi=C_1\Phi_1+C_2\Phi_2+C_3\Phi_3+C_4\Phi_4+C_5\Phi_5, \qquad \text{(A1)}$$

where the C_i are numerical coefficients and each Φ_i is a certain linear combination of the Slater determinants built from atomic orbitals on the carbon nucleus.

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[10] This may be compared with the value quoted by C. A. Coulson, 4.06 D, in remarks presented at the Shelter Island Conference of 1951.

[11] K. Ruedenberg, Rev. Mod. Phys. **34**, 326 (1962). However, although the charge may be more clustered about H in CH_4 than in C+4 H, the net charge at H may be less in CH_4.

[12] For example, P.-O. Löwdin and H. Shull, Phys. Rev. **101**, 1730 (1956).

[13] For example, W. C. Hamilton, J. Chem. Phys. **26**, 345 (1957).

[14] M. Krauss, J. Chem. Phys. **38**, 564 (1963).

[15] Very recent papers that shed further light on the questions here discussed include the following: J. T. Sinai, J. Chem. Phys. **39**, 1575 (1963); W. T. King, J. Chem. Phys. **39**, 2141 (1963); E. L. Albasiny and J. R. A. Cooper, Proc. Phys. Soc. (London) **82**, 289 (1963).

Namely, in a standard notation,

$$\Phi_1=(s\bar{s}s^*\bar{s}^*p_x\bar{p}_xp_y\bar{p}_yp_z\bar{p}_z),$$

$$\Phi_2=6^{-\frac{1}{2}}[(s\bar{s}s^*\bar{s}^*p_x\bar{d}_{yz}p_y\bar{p}_yp_z\bar{p}_z)+5\text{ other determinants}],$$

$$\Phi_3=2^{-\frac{1}{2}}[(s\bar{s}s^*\bar{f}_{xyz}p_x\bar{p}_xp_y\bar{p}_yp_z\bar{p}_z)+(s\bar{s}f_{xyz}\bar{s}^*p_x\bar{p}_xp_y\bar{p}_yp_z\bar{p}_z)],$$

$$\Phi_4=6^{-\frac{1}{2}}[(s\bar{s}s^*\bar{s}^*p_x\bar{f}_{x(5x^2-3)}p_y\bar{p}_yp_z\bar{p}_z)$$
$$+5\text{ other determinants}],$$

$$\Phi_5=6^{-\frac{1}{2}}[(s\bar{s}s^*\bar{s}^*p_x\bar{g}_{yz(7x^2-1)}p_y\bar{p}_yp_z\bar{p}_z)$$
$$+5\text{ other determinants}].\qquad\text{(A2)}$$

Here each term enclosed in parentheses is a normalized 10×10 determinant made up from the indicated atomic orbitals, with spin function β or spin function α according as there is or is not a bar over the orbital symbol. The Slater atomic orbitals, s, $s'[s^*=(s'-Ss)/(1-S^2)^{\frac{1}{2}}]$, p_x, p_y, p_z, d_{yz}, f_{xyz}, $f_{x(5x^2-3)}$, $g_{yz(7x^2-1)}$, etc., each have a characteristic principal quantum number n and orbital exponent ζ; a typical orbital has the radial part $Ar^{n-1}\exp(-\zeta r)$, where A is a normalizing constant. The five (four independent) linear coefficients C_i, the seven different parameters n, and the seven different parameters ζ, all have been determined by the variational method, for an assumed carbon–hydrogen distance of 2.0 a.u.

The charge density at a point (r, θ, ϕ) is given by Eq. (1) of the text. With the Ψ of Eq. (A1), this may be written

$$\rho(r,\theta,\phi)=\sum_{j=1}^{14}D_j\varphi_j(r,\theta,\phi),\qquad\text{(A3)}$$

where

$$\varphi_1=s(1)s(1),$$
$$\varphi_2=s^*(1)s^*(1),$$
$$\varphi_3=p_x^2(1)+p_y^2(1)+p_z^2(1),$$
$$\varphi_4=d_{xy}^2(1)+d_{xz}^2(1)+d_{yz}^2(1),$$
$$\varphi_5=f_{xyz}^2(1),$$
$$\varphi_6=f_{x(5x^2-3)}^2(1)+f_{y(5y^2-3)}^2(1)+f_{z(5z^2-3)}^2(1),$$
$$\varphi_7=g_{xy(7z^2-1)}^2(1)+g_{xy(7y^2-1)}^2(1)+g_{yz(7x^2-1)}(1),$$
$$\varphi_8=p_x(1)d_{yz}(1)+p_y(1)d_{xz}(1)+p_z(1)d_{xy}(1),$$
$$\varphi_9=s^*(1)f_{xyz}(1),$$
$$\varphi_{10}=p_x(1)f_{x(5x^2-3)}(1)+p_y(1)f_{y(5y^2-3)}(1)$$
$$+p_z(1)f_{z(5z^2-3)}(1),$$
$$\varphi_{11}=p_x(1)g_{yz(7x^2-1)}(1)+p_y(1)g_{xz(7y^2-1)}(1)$$
$$+p_z(1)g_{xy(7z^2-1)}(1),$$
$$\varphi_{12}=d_{yz}(1)f_{x(5x^2-3)}(1)+d_{xz}(1)f_{y(5y^2-3)}(1)$$
$$+d_{xy}(1)f_{z(5z^2-3)}(1),$$
$$\varphi_{13}=d_{yz}(1)g_{yz(7x^2-1)}(1)+d_{xz}(1)g_{xz(7y^2-1)}(1)$$
$$+d_{xy}(1)g_{xy(7z^2-1)}(1),$$
$$\varphi_{14}=f_{x(5x^2-3)}(1)g_{yz(7x^2-1)}(1)+f_{y(5y^2-3)}(1)g_{xz(7y^2-1)}(1)$$
$$+f_{z(5z^2-3)}(1)g_{xy(7z^2-1)}(1),\qquad\text{(A4)}$$

and

$$D_1=2C_1^2+2C_2^2+2C_3^2+2C_4^2+2C_5^2=2,$$
$$D_2=2-C_3^2,\qquad D_3=2-\tfrac{1}{3}(C_2^2+C_4^2+C_5^2),$$
$$D_4=\tfrac{1}{3}C_2^2,\qquad D_5=C_3^2,\qquad D_6=\tfrac{1}{3}C_4^2,$$
$$D_7=\tfrac{1}{3}C_5^2,\qquad D_8=\tfrac{2}{3}(6)^{\frac{1}{2}}C_1C_2,\qquad D_9=2(2)^{\frac{1}{2}}C_1C_3,$$
$$D_{10}=\tfrac{2}{3}(6)^{\frac{1}{2}}C_1C_4,\qquad D_{11}=\tfrac{2}{3}(6)^{\frac{1}{2}}C_1C_5,\qquad D_{12}=\tfrac{2}{3}C_2C_4,$$
$$D_{13}=\tfrac{2}{3}C_2C_5,\qquad D_{14}=\tfrac{2}{3}C_4C_5.\qquad\text{(A5)}$$

Each of the φ_j may be expressed as a function of r only, $R_j(r)$ (except for φ_2 and φ_9 this is the product of the normalized radial parts of two orbitals), times a function of θ and ϕ only, $Z_j(\theta, \phi)/4\pi$ (this is a product or sum of products of the normalized angular parts of two orbitals):

$$\varphi_j(r,\theta,\phi)=R_j(r)[Z_j(\theta,\phi)/4\pi].\qquad\text{(A6)}$$

Thus

$$4\pi\rho(r,\theta,\phi)=\sum_{j=1}^{14}B_j(r)Z_j(\theta,\phi),\qquad\text{(A7)}$$

where

$$B_j(r)=D_jR_j(r).\qquad\text{(A8)}$$

A more compact form for ρ is obtained if use is made of the fact that it must be totally symmetric under all operations of the tetrahedral group. This means that the functions $Z_j(\theta, \phi)$ which enter Eq. (A7) must be expressible as linear combinations of the totally symmetric tetrahedral harmonics $T_l(\theta, \phi)$ given in Table I of the text. In terms of these one has

$$Z_1=T_0,\qquad Z_2=T_0,\qquad Z_3=3T_0,$$

$$Z_4=3T_0-\frac{2(21)^{\frac{1}{2}}}{7}T_4,\qquad Z_5=T_0-\frac{2(21)^{\frac{1}{2}}}{11}T_4+\frac{20(26)^{\frac{1}{2}}}{143}T_6,$$

$$Z_6=3T_0+\frac{3(21)^{\frac{1}{2}}}{11}T_4+\frac{25(26)^{\frac{1}{2}}}{143}T_6,$$

$$Z_7=3T_0-\frac{27(21)^{\frac{1}{2}}}{77}T_4+\frac{15(26)^{\frac{1}{2}}}{143}T_6,$$

$$Z_8=\frac{3(21)^{\frac{1}{2}}}{7}T_3,\qquad Z_9=T_3,\qquad Z_{10}=2T_4,$$

$$Z_{11}=\frac{6(7)^{\frac{1}{2}}}{7}T_3,\qquad Z_{12}=-2T_3,$$

$$Z_{13}=-\frac{30(7)^{\frac{1}{2}}}{77}T_4+\frac{30(78)^{\frac{1}{2}}}{143}T_6,$$

$$Z_{14}=-\frac{3(3)^{\frac{1}{2}}}{11}T_3+\frac{35(39)^{\frac{1}{2}}}{143}T_7.\qquad\text{(A9)}$$

If these relations are written

$$Z_j(\theta,\phi)=\sum_{l=1}^{7}A_{jl}T_l(\theta,\phi),\qquad\text{(A10)}$$

TABLE V. Values of certain integrals $U(p, q, r)$.[a,b]

	$q=0$	1	2	3	4	5	6	7	8
$r=0$, $p=0$	261 799	54 942	16 825	6086	2422	1025	454	207	97
1	120 150	27 189	8652	3202	1294	554	247	114	54
2	61 483	14 288	4623	1731	705	304	136	63	30
3	33 427	7809	2540	955	391	169	76	35	17
4	18 903	4389	1425	536	219	95	43	20	9
5	10 993	2520	813	304	124	54	24	11	5
6	6530	1472	470	175	71	31	14	6	3
7	3945	872	275	102	41	18	8	4	2
8	2416	523	163	60	24	10	5	2	1
$r=1$, $p=0$	217 605	96 225	48 034	25 660	14 323	8248	4862	2919	1779
1	43 252	20 833	10 740	5787	3218	1832	1064	627	374
2	12 735	6415	3376	1833	1019	577	332	193	114
3	4471	2315	1236	675	376	212	121	70	41
4	1738	916	494	272	151	85	49	28	16
5	722	386	210	116	65	36	21	12	7
6	314	170	93	51	29	16	9	5	3
7	142	77	42	24	13	7	4	2	1
8	66	36	20	11	6	4	2	1	1

[a] See text and Eq. (A19) for definition of $U(p, q, r)$.

[b] Tabulated are values of $U(p, q, r)\times 10^6$.

then Eq. (A7) becomes

$$4\pi\rho(r,\theta,\phi)=\sum_{l=1}^{7}A_l(r)\,T_l(\theta,\phi), \qquad \text{(A11)}$$

where

$$A_l(r)=\sum_{j=1}^{14}A_{jl}B_j(r). \qquad \text{(A12)}$$

Equation (A11) is the final working formula for the electron density, Eq. (3) of the text.

As examples of Eq. (A12), the first two nonvanishing $A_l(r)$ are given by the formulas,

$$\begin{aligned}A_0(r)=2R_1(r)+2R_2(r)+6R_3(r)+C_2^2[R_4(r)-R_3(r)]\\+C_3^2[R_5(r)-R_2(r)]+C_4^2[R_6(r)-R_3(r)]\\+C_5^2[R_7(r)-R_3(r)] \qquad \text{(A13)}\end{aligned}$$

and

$$\begin{aligned}A_3(r)=\tfrac{6}{7}(14)^{\frac{1}{2}}C_1C_2R_8(r)+2(2)^{\frac{1}{2}}C_1C_3R_9(r)\\+\tfrac{4}{7}(42)^{\frac{1}{2}}C_1C_5R_{11}(r)-\tfrac{4}{5}C_2C_4R_{12}(r)\\-\tfrac{2}{11}(3)^{\frac{1}{2}}C_4C_5R_{14}(r). \qquad \text{(A14)}\end{aligned}$$

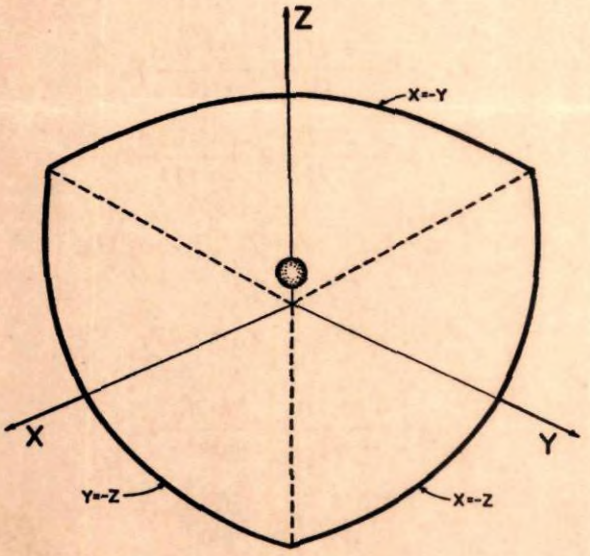

FIG. 8. A tetrant. Pictured is the equilateral spherical triangle of area π associated with a typical hydrogen atom, the second from the top in Fig. 1.

APPENDIX II. CERTAIN INTEGRALS OVER THE UNIT SPHERE

Two groups of integrals were needed for the present work, integrals over all or part of the unit sphere of various powers of the Cartesian coordinates of a point on the unit sphere.

$$x=\sin\theta\cos\phi, \qquad y=\sin\theta\sin\phi, \qquad z=\cos\theta. \qquad \text{(A15)}$$

The integrals are

$$S(p,q,r)=\iint_{\text{whole sphere}}x^py^qz^r d\Omega \qquad \text{(A16)}$$

and

$$T(p,q,r)=\iint_{\text{one tetrant}}x^py^qz^r d\Omega, \qquad \text{(A17)}$$

where "one tetrant" is the quarter sphere associated with the proton located at $x=y=z=1/(3)^{\frac{1}{2}}$, that is, the spherical triangle of area π bounded by great circles, $x=-z$, $y=-x$, and $z=-x$, as shown in Fig. 8.

The integrals of Eq. (A16) are elementary; they are given by the formula

$$S(p,q,r)=\begin{cases}0 & \text{if } p,\ q, \text{ and } r \text{ are not all even,}\\ 2\Gamma(\tfrac{1}{2}p+\tfrac{1}{2})\Gamma(\tfrac{1}{2}q+\tfrac{1}{2})\Gamma(\tfrac{1}{2}r+\tfrac{1}{2})/\Gamma(\tfrac{1}{2}p+\tfrac{1}{2}q+\tfrac{1}{2}r+\tfrac{3}{2}) & \\ & \text{if } p,\ q, \text{ and } r \text{ are all even,}\end{cases}\tag{A18}$$

where $\Gamma(n)$ is the gamma function of n. For example, $S(0,\ 0,\ 0)=2[\Gamma(\frac{1}{2})]^3/\Gamma(\frac{3}{2})=2[\pi^{\frac{1}{2}}]^3/[1/2\pi^{\frac{1}{2}}]=4\pi$, the area of the unit sphere. These integrals are useful for the verification of the orthonormalization conditions, Eq. (4) of the text, for the tetrahedral harmonics listed in Table I.

The integrals over the individual tetrant are more difficult. These may be compounded from individual integrals over $\frac{1}{48}$ of the unit sphere,

$$U(p,q,r)=\int_{y=0}^{1/(3)^{\frac{1}{2}}}\int_{x=y}^{[(1-y^2)/2]^{\frac{1}{2}}}x^py^qz^rd\Omega$$

$$=\int_0^{1/(3)^{\frac{1}{2}}}y^qdy\int_y^{[(1-y^2)/2]^{\frac{1}{2}}}x^p(1-x^2-y^2)^{(r-1)/2}dx.\tag{A19}$$

Namely,

$$\begin{aligned}T(p,q,r)=&[1+(-1)^p][U(q,p,r)+U(r,p,q)]\\&+[1+(-1)^q][U(p,q,r)+U(r,q,p)]\\&+[1+(-1)^r][U(p,r,q)+U(q,r,p)].\end{aligned}\tag{A20}$$

The integrals $U(p,\ q,\ r)$, for p and q having values from 0 to 8 and r having the values 0 and 1, are given in Table V.

Calculation of the $U(p,\ q,\ r)$ may be accomplished making use of the following recursion scheme. Any $U(p,\ q,\ r)$ first may be expressed in terms of the $U(p,\ q,\ 0)$ or the $U(p,\ q,\ 1)$ using

$$\begin{aligned}U(p,q,r)=U(p,q,r-2)-U(p+2,q,r-2)&\\-U(p,q+2,r-2).&\end{aligned}\tag{A21}$$

The integrals $U(p,\ q,\ 1)$ can be obtained from the formula

$$\begin{aligned}U(p,q,1)=(p+1)^{-1}\{(\tfrac{1}{2})^{(p+3)/2}B_{\frac{1}{3}}(\tfrac{1}{2}q+\tfrac{1}{2},\tfrac{1}{2}p+\tfrac{3}{2})&\\-(p+q+2)^{-1}(\tfrac{1}{3})^{(p+q+2)/2}\},&\end{aligned}\tag{A22}$$

where

$$B_x(m,n)=\int_0^x t^{m-1}(1-t)^{n-1}dt$$

is an incomplete beta function of the indicated arguments. Finally the integrals $U(p,\ q,\ 0)$ can be obtained from the formula

$$\begin{aligned}U(p,q,0)=&p^{-1}(\tfrac{1}{2})^{\frac{1}{2}p+1}\\&\times\{(\tfrac{1}{2})^{q/2}B_{\frac{1}{2}}(\tfrac{1}{2}p+\tfrac{1}{2}q,\tfrac{3}{2})-B_{\frac{1}{3}}(\tfrac{1}{2}q+\tfrac{1}{2},\tfrac{1}{2}p+1)\}\\&+[(p-1)/p]\{U(p-2,q,0)-U(p-2,q+2,0)\},\end{aligned}\tag{A23}$$

and values of $U(0,\ q,\ 0)$ and $U(1,\ q,\ 0)$; these last are found by Weddle's rule numerical integration procedures.

The relationship between the integrals $S(p,\ q,\ r)$ and the integrals $T(p,\ q,\ r)$ is

$$2S(p,q,r)=[1+(-1)^p][1+(-1)^q][1+(-1)^r]T(p,q,r).\tag{A24}$$

Thus, from Table V and Eqs. (A20) and (A24), $T(0,\ 0,\ 0)=16U(0,\ 0,\ 0)$ and $S(0,\ 0,\ 0)=48U(0,\ 0,\ 0)=48(0.261799)=12.566=4\ \pi$.