Theoret. chim. Acta (Berl.) 17, 384—395 (1970)

Determination of the Charge Distribution of Methane by a Method of Density Constraints

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Received October 24, 1969

The molecular charge distribution of methane is expressed in terms of an orthonormal set of molecular orbitals which are determined solely by imposing a set of constraints on the derived one-electron charge density, the constraints being that the charge density reproduce the experimental expectation values of a set of one-electron operators. The molecular orbitals are expanded in terms of an SCF set of atomic orbitals on carbon and a single 1*s* STO on each hydrogen. The derived charge distribution is found to be equal to the SCF Hartree-Fock distribution in its prediction of one-electron expectation values. The energy, as determined by the associated wave function, is -40.156 a.u. This energy value is comparable to that obtained in a SCF LCAO MO calculation with a similar basis set and is 0.048 a.u. above the best calculated value of the Hartree-Fock limit.

Die molekulare Ladungsverteilung des Methans wird mit Hilfe eines orthogonalen Satzes von Molekülorbitalen ausgedrückt, die lediglich durch eine Reihe von Nebenbedingungen an die Einelektronen-Ladungsdichte bestimmt sind. Die Nebenbedingungen bestehen darin, daß die Ladungsdichte die experimentellen Erwartungswerte eines Satzes von Einelektronen-Operatoren reproduzieren soll. Die Molekülorbitale werden nach einem Satz von atomaren SCF-Orbitalen am Kohlenstoff sowie einem einzigen 1*s* STO an jedem Wasserstoffatom entwickelt. Man findet, daß die erhaltene Ladungsverteilung der SCF-Hartree-Fock-Verteilung bezüglich der Bestimmung von Einelektronen-Erwartungswerten gleichkommt. Die Energie, die aus der zugehörigen Wellenfunktion bestimmt wird, ist $-40{,}156$ a.u. Dieser Energiewert ist mit demjenigen, der in SCF LCAO MO-Berechnungen mit einem ähnlichen Basissatz bestimmt wird, vergleichbar und liegt 0,048 a.u. über dem besten berechneten Wert der Hartree-Fock-Grenze.

La distribution de charge moléculaire du méthane est exprimée au moyen d'un ensemble orthonormé d'orbitales moléculaires déterminées uniquement à l'aide d'une série de contraintes sur les densités de charge obtenues, à savoir que ces densités reproduisent les valeurs expérimentales des valeurs moyennes de différents opérateurs monoélectroniques. Les orbitales moléculaires sont développées en orbitales atomiques SCF sur le carbone et en orbitale de Slater 1*s* sur chaque hydrogène. La distribution de charge obtenue est trouvée égale à la distribution SCF Hartree-Fock dans les prévisions des valeurs moyennes d'opérateurs monoélectroniques. L'énergie, déterminée à l'aide de la fonction d'onde associée, est -40.156 u.a. Cette valeur de l'énergie est comparable à celle obtenue dans un calcul SCF LCAO MO avec une base similaire et est située à 0,048 u.a. au dessus de la meilleure évaluation de la limite Hartree-Fock.

Introduction

We wish to demonstrate that by requiring the one-electron charge density $\varrho(\boldsymbol{x})$ to reproduce the mean values $\langle \Omega_n(\boldsymbol{x}) \rangle$ of as many independent one-electron operators $\Omega_n(\boldsymbol{x})$ as there are independent parameters in $\varrho(\boldsymbol{x})$, one may obtain,

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in favourable cases, a molecular charge distribution superior to that obtained by the usual energy minimization procedure. With a given basis set the latter procedure yields the best possible description of the two-electron distribution function, but not necessarily the best one-electron distribution function. This was clearly demonstrated by Mukherji and Karplus [1] who performed a regular SCF calculation and compared the results obtained with those of a second calculation performed with two additional Lagrangian multipliers, the additional undetermined multipliers resulting from the constraints that the wave function yield the correct dipole moment and quadrupole coupling constant. The constrained wave function was found to yield more accurate values for other one-electron properties than the unconstrained function with only a slight increase in the energy.

In the present work no energy minimization is employed and the charge density is determined directly by the requirement that it reproduce the observed values of properties which are themselves functions of the one-electron charge distribution. This method was proposed and applied previously to hydrogen fluoride and ammonia [2, 3]. Only simple minimal basis sets were employed in the expansion of the charge density in these cases but a comparison of the one-electron properties thus calculated with those determined from an SCF calculation employing comparable basis sets demonstrated the possibilities of the method.

Recent SCF results for molecules containing third-row atoms, those of Matcha [4, 5] for LiCl and NaCl for example, indicate a deterioration in the accuracy of the computed values of the one-electron properties compared to the calculations for molecules containing second-row atoms. This decrease in the accuracy of the molecular charge distribution derived from an SCF calculation is not too surprising since the core orbitals of the larger molecules, because of their very large contributions to the total energy, exert a dominant effect in determining the variational parameters. The result is that as the molecular size increases the core density is accurately determined but the valence density, because of its much smaller contribution to the energy, is less accurately determined. The SCF results for third- and fourth-row atoms do not suffer from this defect because of the high symmetry of the potential field in the atomic case.

In the present approach operators whose mean values are heavily weighted in regions of space dominated by the valence density are included in the set of constraints. For example, the molecular charge distribution of methane is determined by requiring $\varrho(\boldsymbol{x})$ to balance the nuclear force of repulsion on the protons and yield the correct value for the diamagnetic contribution to the proton shielding constant. The primary role of the core density on carbon (or on Si in SiH_4) in the determination of the forces is to simply shield an equivalent number of nuclear charges on the carbon nucleus from the protons. In addition, in this favourable case of high symmetry the first possible polarization of the core density is an octupolar one. Hence the variations in the charge density required to satisfy the force constraint are restricted to the valence components.

Calculation of the Charge Density

The coordinate system is such that the methane molecule is inscribed in a cube of side $2a$ where $a = R/\sqrt{3}$ (R = C–H equilibrium bond length of 2.06172 a.u. [6]) and the coordinates of the carbon and four hydrogen nuclei are respectively $(0, 0, 0)$, (a, a, a), $(a, \bar{a}, \bar{a})$, $(\bar{a}, a, \bar{a})$ and $(\bar{a}, \bar{a}, a)$. The molecular charge distribution is expanded in terms of a basis set consisting of Clementi's [7] SCF atomic orbitals for the ^3P state of carbon and a single Slater orbital with an exponent of 1.5 centered on each of the protons. This value for the orbital exponent on hydrogen was necessary to satisfy simultaneously the force and diamagnetic shielding constraints. The orbital coefficients in Woznick's wave function for methane [8] which included hydrogen $1s$ orbitals with exponents of both 1.0 and 1.5 show the orbital with exponent 1.5 to be the dominant one at the equilibrium value of R.

The molecular charge distribution is expressed in terms of an inner shell orbital ϕ_0 on carbon which is set equal to Clementi's [7] SCF $1s$ orbital for carbon and four equivalent bonding orbitals

$$\phi_{bi} = \lambda(\cos\varepsilon_b 2s_C + \sin\varepsilon_b p_i) + \mu(h_i - \delta[h_j + h_k + h_l]) - c_0 1s_C \tag{1}$$

where the h_i are the Slater orbitals on the hydrogens and the $1s_C, 2s_C$ and p_i are SCF atomic functions for carbon. The p_i are normalized linear combinations of $2p_x$, $2p_y$ and $2p_z$ orbitals, each directed at one of the protons. The constant c_0

$$c_0 = \langle h_i | 1s_C \rangle (1 - 3\delta) + \lambda/\mu \cos\varepsilon_b \langle 1s_C | 2s_C \rangle$$

insures orthogonality of the inner shell with the bonding orbitals. The parameters appearing in the expression for the ϕ_{bi} have the following physical significance: λ/μ is a bond polarity factor, ε_b is an s-p hybridization parameter for the directed orbital from carbon, and δ determines the extent of delocalization in the equivalent orbitals. The molecular charge density $\varrho(\boldsymbol{x})$ is given by

$$\varrho(\boldsymbol{x}) = 2\left(\phi_0^2 + \sum_i \phi_{bi}^2\right). \tag{2}$$

The normalization and orthogonality conditions

$$\int \phi_{bi}\phi_{bj} d\tau = \delta_{ij} \tag{3}$$

can be used to determine two of the four unknown parameters λ, μ, ε_b and δ appearing in the generalized set of equivalent orbitals. The two remaining parameters are obtained by requiring the total density distribution to give a zero resultant force on the proton and to yield the experimental value of the diamagnetic contribution to the proton magnetic shielding $\sigma^{(d)}$. Thus in addition to the set of SCF orbitals for carbon the input information consists of the experimental geometry of the methane molecule and the experimental value of $\sigma^{(d)}$.

The geometry of the molecule determines the nuclear force of repulsion on the proton F^N which must be balanced by the electrostatic force F^e exerted by the molecular charge density

$$F^{N} = (Z_C + 3/(4 \cos\alpha))/R^2 = 1.6276 \text{ a.u.}$$

where Z_C is the nuclear charge on carbon and α is the angle formed between a C–H bond and a diagonal in the face of the cube joining the positions of two protons. The electronic force on the proton is determined by the mean value of the operator $\cos\theta_H/r_H^2$

$$F^{e} = -\langle \cos\theta_H/r_H^2 \rangle$$

where θ_H is measured from the C–H bond axis and r_H is a radial coordinate centred on the proton in question.

Ramsey [9] has shown that the proton magnetic shielding constant σ consists of diamagnetic and paramagnetic contributions

$$\sigma = \sigma^{(d)} + \sigma^{(p)} .$$

Using the experimental value of the proton spin-rotation constant obtained from molecular beam studies [10] and equal to 10.40 ± 0.10 kc/sec, $\sigma^{(p)}$ is determined to be -56.45×10^{-6} emu [11] at the equilibrium bond length. The total proton magnetic shielding is obtained by adding the value for the proton shielding [12] in H_2 ($26.43 \pm 0.60 \times 10^{-6}$) to the observed [13] proton shift 4.20×10^{-6} between methane and H_2. This gives

$$\sigma = 30.63 \pm 0.60 \times 10^{-6} \text{ emu}$$

and

$$\sigma^{(d)} = 87.0 \times 10^{-6} \text{ emu} .$$

The value of $\sigma^{(d)}$ is determined by the mean value of the operator $1/r_H$

$$\sigma^{(d)} = (e^2/3mc^2) \langle 1/r_H \rangle .$$

The conditions imposed by Eq. (3) are used to obtain analytic expressions for ε_b and λ which can be solved for assigned values of μ and δ. In an actual calculation, δ is assigned an arbitrary value, μ is set equal to some initial value and λ and ε_b are calculated for these values of δ and μ. The parameter μ is varied until the electronic and nuclear forces on the proton are balanced and the proton magnetic shielding $\sigma^{(d)}$ is calculated. If the calculated value of $\sigma^{(d)}$ does not equal the experimental value for this property a new value is assigned to δ and the procedure is repeated. By this relatively simple procedure δ and μ were varied until both the one-electron constraints were satisfied [14].

The final values of the orbital parameters and the resulting values of F^{e} and $\sigma^{(d)}$ are recorded in Table 1. The expression characterizing the bonding orbitals is

$$\phi_{bi} = 0.39011176(2s_C) + 0.61388699(p_i) - 0.012828560(1s_C)$$

$$+ 0.36865974(h_i) - 0.044754370(h_j + h_k + h_l) .$$

The basis set employed is flexible enough to simultaneously satisfy the two constraints and the orthogonality and normalization restrictions to eight significant figures.

Table 1. *Values of the orbital parameters and one-electron constraints*

δ	μ	λ	ε_b	Electronic force (a.u.)[a]	$\sigma^{(d)}$ (a.u.)[a]
0.12139750	0.36865974	0.72735440	57.564934°	−1.62763213	4.90588209

[a] The values of the two constraints from the experimental data (given to nine significant figures for the purpose of the calculation) are $F^e = -1.62763214$ a.u. and $\sigma^{(d)} = 4.90588209$ a.u.

Examination and Comparison of the Derived Wave Function and Charge Distribution

The expectation values of the energy and three one-electron properties, the diamagnetic susceptibility, the octupole moment and the field gradient at the proton, for a number of methane wave functions are collected in Table 2 for comparison with the presently derived results. In all cases but the first the wave function is represented by a single Slater determinant. The first two wave functions are representative of one-centre calculations, that of Moccia [16] being the best of such calculations for methane in terms of the energy criterion. The following two are SCF LCAO MO calculations employing Gaussian basis sets, the function of Ritchie and King [18] yielding an energy close to the Hartree-Fock limit. The four final functions are the results of SCF LCAO MO multicentre calculations using progressively larger basis sets of Slater type orbitals. The function of Arrighini *et al.* [20] using 39 STO is estimated to be within 0.02 au of the Hartree-Fock energy for methane. The same authors also computed a wave function for methane using a basis set of the same size (22 STO) and of approximately the same composition as that employed in the present work.

Energy

The wave function derived in the present work without the use of energy minimization yields an energy of −40.156 a.u. This estimate of the energy of methane is considerably better than that obtained by any of the one-centre calculations and is only 0.048 a.u. above the best value so far obtained for methane by Arrighini *et al.* [20] using a basis set of 39 STO's with partial optimization of the exponents. Reference to Table 2 shows that the present value of the energy compares favourably with that obtained by Arrighini *et al.* [20] in their SCF calculation using a comparable basis set of 22 STO. The value obtained for V/T in the present case is −1.9886.

One-Electron Properties

The diamagnetic contribution to the magnetic susceptibility is related to the mean value of r_C^2 by

$$\chi^{(d)} = -\frac{N_0 e^2}{6mc^2}\langle r_C^2\rangle .$$

While most of the calculated values reported in Table 2 are close to the experimental value, the presently derived charge density is the most contracted

Table 2. *Comparison of energy and one-electron properties for* CH_4 *wave functions*

Ref.	Method of calc.	$\chi^{(d)}$ (cgs ppm)	$-\sqrt{15}\,\langle x_C y_C z_C\rangle$ (a.u.)	I_3 (a.u.)	eqQ/h (kc/sec)	Energy (a.u.)
[15]	one centre, SCF 5 detor, $l \leqq 5$		-11.00	$+12.85$		-39.844
[16]	one centre, SCF $l \leqq 3$, 26 STO					-39.866
[17]	SCF LCAO MO 33 GTO		-22.464	$+\ 3.847$		-40.167
[18]	SCF LCAO MO 52 GTO					-40.198
[19]	SCF LCAO MO 9 STO	-27.9			224	-40.128
[8]	SCF LCAO MO 27 STO	-28.7	-23.099	$+\ 3.212$		-40.181
[20]	SCF LCAO MO 22 STO	-27.84	-20.691	$+\ 5.655$	216.7	-40.178
[20]	SCF LCAO MO 39 STO	-29.97	-21.805	4.541	207.7	-40.204
present	density constraint 22 STO	-27.17	-16.500	9.628	196.1	-40.156
Exp.		-26.71 [20, 21]		9.796 [22]		-40.525 [18]

and gives the best agreement with experiment. Obviously, the mean value of $\langle r_C^2\rangle$ could have been used along with $\langle \cos\theta_H/r_H^2\rangle$ as a constraint on the density in place of $\langle 1/r_H\rangle$ without significantly changing the final result. The necessity of using an exponent of 1.5 for the hydrogen orbitals to satisfy the $\langle 1/r_H\rangle$ constraint is one of the principle factors contributing to the contracted nature of the charge density and consequently to a very nearly correct prediction of $\langle r_C^2\rangle$.

The only non-vanishing component of the electronic octupole moment is given by the mean value of $-\sqrt{15}\,x_C y_C z_C$ and the total moment, electronic plus nuclear, is [21]

$$I_3 = -\sqrt{15}\,\langle x_C y_C z_C\rangle + \sqrt{15}\,\Sigma_\alpha Z_\alpha x_\alpha y_\alpha z_\alpha\,.$$

Table 2 lists values of both the total moment and its electronic contribution.

The charge distribution determined by the present method yields a value for the octupole moment which is in close agreement with the recommended value for this property [22]. The estimates of I_3 from the multicentre SCF calculations are uniformly lower than this value. The one-centre calculation of Parr *et al.* [15] employing a basis set with values of $l \leqq 5$ and expressed as a linear combination of five determinantal functions gives a value for I_3 slightly larger than the one calculated here.

The electric field gradient at the proton

$$q_e = \langle (3\cos^2\theta_H - 1)/r_H^3 \rangle$$

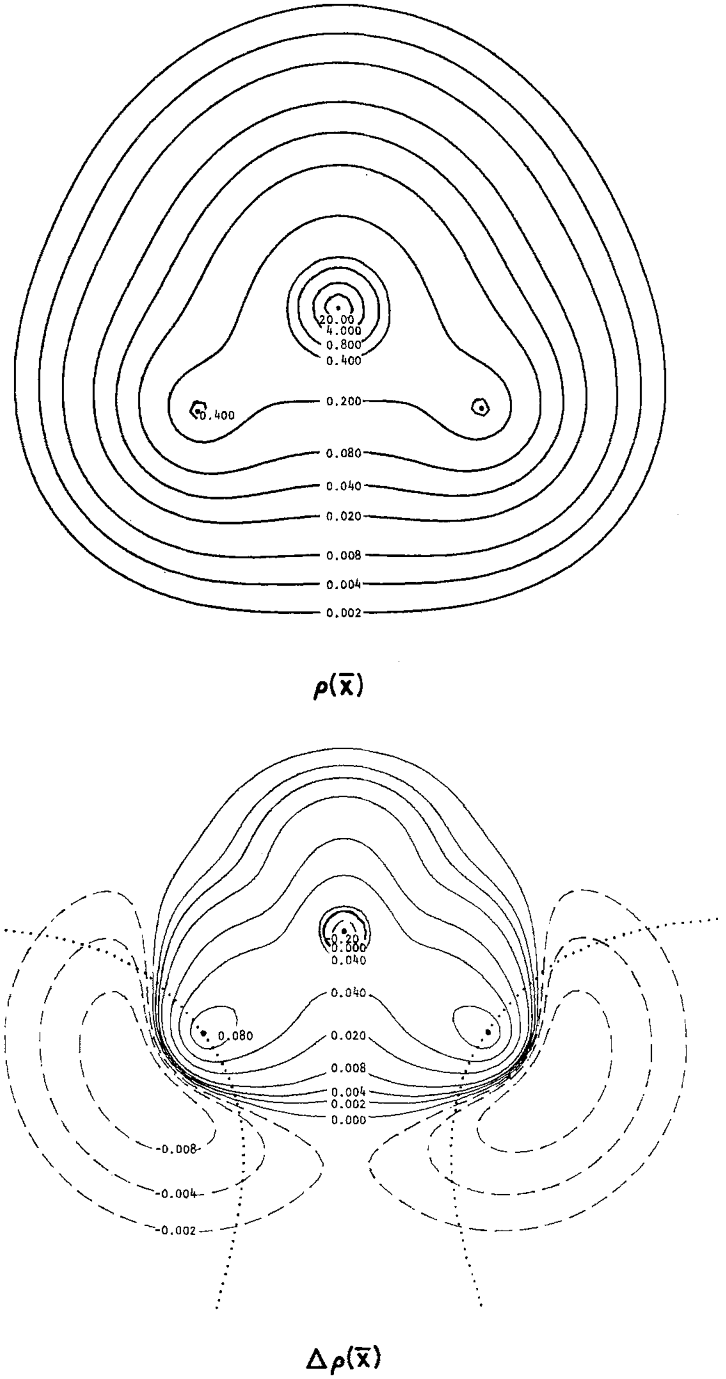
may be related to the deuteron coupling constant eqQ/h, where q is the total electric field gradient at the proton and Q is the deuteron quadrupole moment. The value derived from the present charge distribution of 196.1 kc/sec is in good agreement with the result of Caves and Karplus [23] who estimate this quantity to be 210 ± 30 kc/sec. All the theoretical estimates fall within this suggested range, and all lie outside a very uncertain experimental value of 100 ± 50 kc/sec [24].

The method of one-electron constraints has yielded a molecular charge distribution for methane which is comparable to or superior to the Hartree-Fock function in its prediction of one-electron properties and the corresponding wave function yields an energy comparable to that obtained in an SCF calculation with a basis set of corresponding size. The charge distribution provides acceptable estimates of moments depending on the average values of r_C^3, r_C^2, $1/r_H$, $1/r_H^2$ and $1/r_H^3$. Since each of these moments when averaged over the charge distribution separately measure the accuracy of the wave function in different regions of space, the agreement of their calculated expectation values with experiment indicates that the derived charge distribution should exhibit proper behaviour over all space. The following section, therefore, considers in some detail the three-dimensional spatial distribution of the calculated charge density.

The Spatial Distribution of the Charge Density

The molecular charge distribution of methane $\varrho(\boldsymbol{x})$ is displayed in the form of density contour maps, one in the HCH plane (Fig. 1) and four others in a series of planes perpendicular to one of the three-fold symmetry axes (Fig. 2). Also displayed in each case is the corresponding density difference distribution $\Delta\varrho(\boldsymbol{x})$ which is constructed by subtracting from the molecular charge distribution the densities of the component undistorted atoms fixed at the molecular geometry. The density difference distribution provides a detailed picture of the change in the charge density of the separated atoms accompanying the formation of the molecule. (The SCF atomic density for carbon is sphericalized for the construction of the $\Delta\varrho(\boldsymbol{x})$ map.)

The contour maps of $\varrho(\boldsymbol{x})$ and $\Delta\varrho(\boldsymbol{x})$ indicate that the charge density is strongly directed along the four C–H bond axes and thus the tetrahedral geometry and the associated three-fold symmetries of the molecule are very evident in the spatial distribution of the electronic charge. The contour maps, particularly the $\Delta\varrho(\boldsymbol{x})$ maps in Fig. 2 indicate that the charge distribution in the methane molecule is very contracted relative to the charge densities of the atoms. The increase in charge density in the immediate vicinity of the protons and its decrease at the carbon nucleus as shown in the $\Delta\varrho(\boldsymbol{x})$ maps are typical of the effects found in the formation of an AH bond [25, 26]. In particular, the pattern of charge increase and charge decrease in the region of a proton in CH_4 is similar in magnitude and spatial extent to that found for the proton in a Hartree-Fock $\Delta\varrho(\boldsymbol{x})$ map for the



$\rho(\bar{x})$

$\Delta\rho(\bar{x})$

Fig. 1. Contour maps in an HCH plane of the total charge distribution and the density difference distribution for methane at its equilibrium geometry. The contours are in a.u. (1 a.u. $= 6.749\ e^-/\text{Å}^3$). The dotted lines through the protons are the boundary surfaces between the binding and antibinding regions

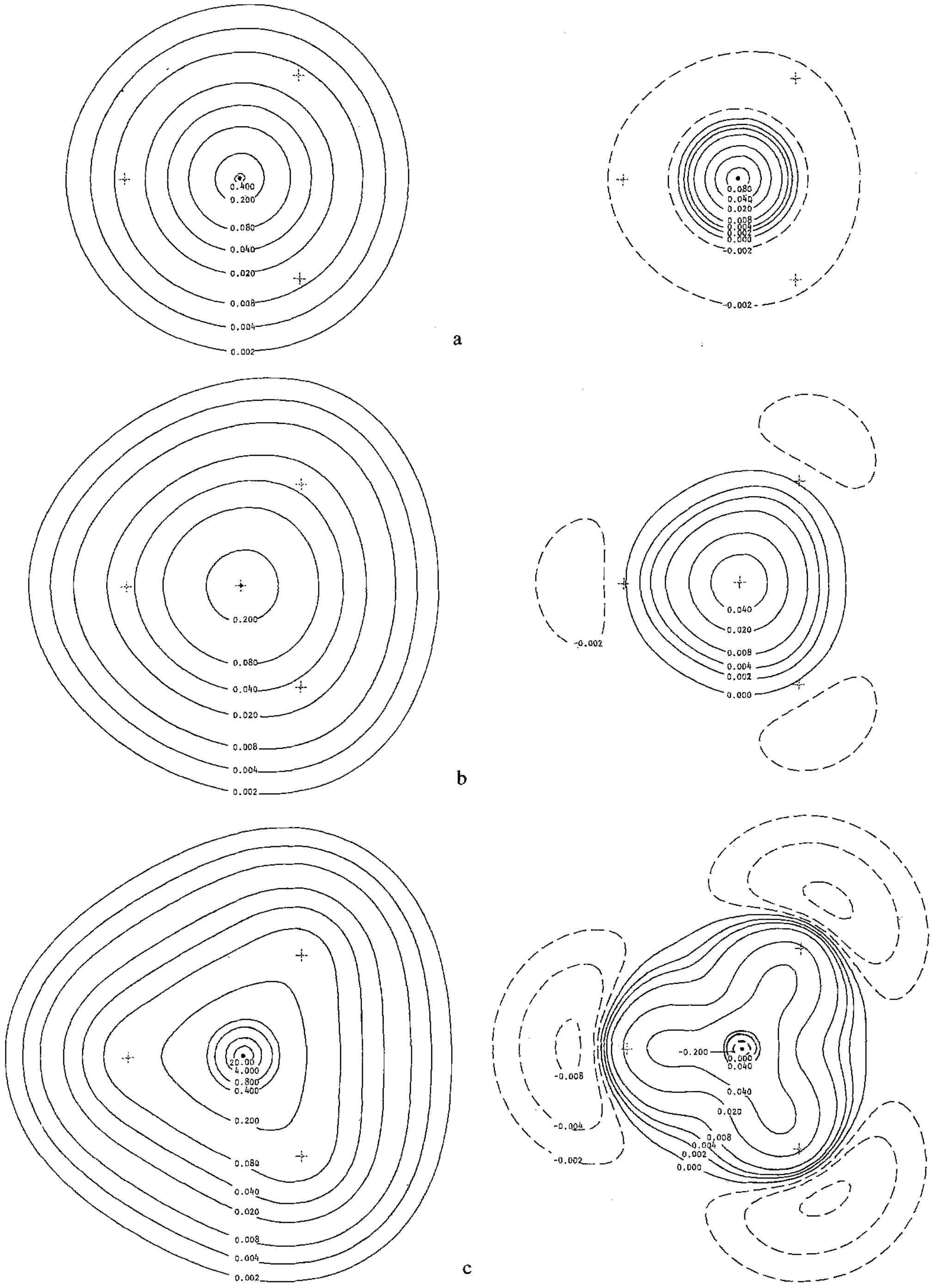


Fig. 2a–d. Contour maps of $\varrho(x, y)$ and $\Delta\varrho(x, y)$ of methane in planes perpendicular to one of the three-fold axes: a) a plane containing the proton on the three-fold axis; b) a plane midway between the C and H nuclei on the three-fold axis; c) a plane containing the C nucleus; and d) a plane containing three H nuclei. The vertical projections of the positions of nuclei not contained in a given plane are indicated by crosses

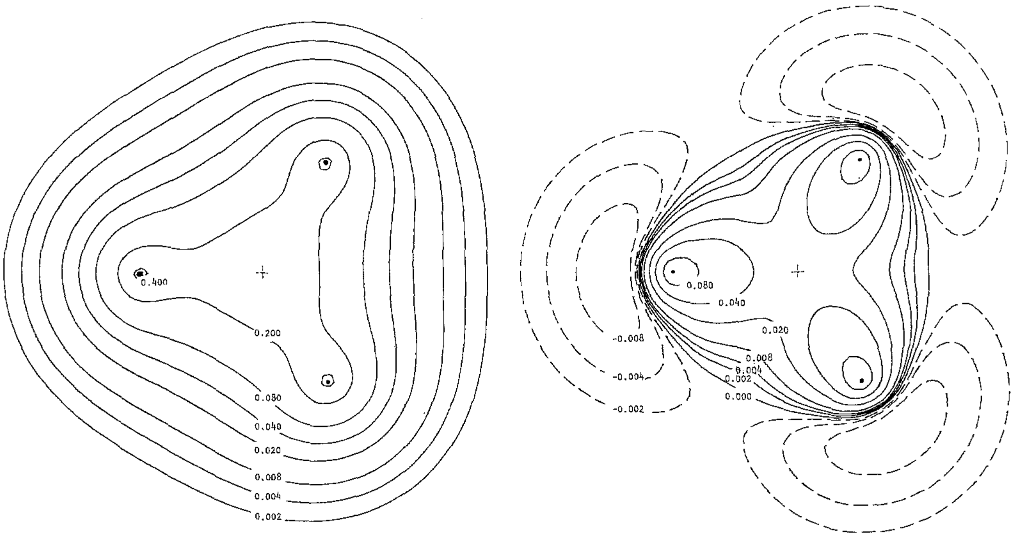


Fig. 2d

CH diatomic molecule [25][1]. Both $\Delta\varrho(\boldsymbol{x})$ maps indicate an increase in charge density at the proton and a decrease at the carbon nucleus. The charge density at the proton in CH_4 is calculated to be 0.5023 a.u., a value slightly higher than the value of 0.4705 a.u. calculated for the proton in the diatomic molecule CH. (The equilibrium bond length in CH is 2.124 a.u. slightly larger than the value of 2.06172 a.u. for CH_4.)

The outermost contour shown in the maps of the total charge distribution (0.002 a.u.) defines a volume in space which contains over 95% of the electronic charge of the system. We have previously shown that the diameter of this contour provides a reasonable estimate of the non-bonded size of the molecule [27]. In the case of methane the diameter of the 0.002 a.u. contour has an average value of 7.6 a.u. The experimental diameter obtained from a Lennard-Jones (6–12) potential in which the parameters are determined by second virial coefficient or viscosity data [28] is 8.1 a.u. The "Lennard-Jones" diameter involves an averaging over the dimensions of a molecule and for spherical atoms or near spherical molecules the 0.001 a.u. contour provides a set of theoretical diameters which are in closer agreement with the experimental values. Examples are (the experimental values are bracketted): CH_4, 8.2 (8.1); He, 5.0 (5.4); Ne, 5.8 (5.9); Ar, 7.5 (7.2), all in a.u.

The present wave function, since it is expressed in terms of localized equivalent orbitals of the type proposed by Lennard-Jones [29], may be used for a discussion of the C–H bond in methane. The small value of the delocalization

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[1] Parr *et al.* [15] have given a $\Delta\varrho(\boldsymbol{x})$ distribution for methane based on a one-centre expansion of the wave function. Their $\Delta\varrho(\boldsymbol{x})$ distribution indicates a decrease in the charge density relative to the atomic distributions in the region of each proton. However, one-centre calculations far underestimate the value of the charge density at the positions of the off-centre nuclei. A comparison of the charge distribution from a one-centre calculation with the Hartree-Fock result for diatomic hydrides [26] indicates that a one-centre calculation underestimates the density in the region of the proton to almost the same extent as does the corresponding united atom density, an error in the range of 80 to 90%.

parameter δ (see Table 1) indicates that the density in each of the equivalent orbitals is largely localized in the region of a single C–H bond. The hybridization parameter ε_b is close in value to 60° indicating that the directed components to the bonding orbitals from carbon are close to sp^3 hybrids, or one-quarter $2s$ and three-quarters $2p$. The bond dipole moment calculated for a single equivalent orbital

$$\mu_{bi} = e(2\langle\phi_{bi}|r_{\mathrm{C}}\cos\theta_{\mathrm{C}}|\phi_{bi}) - R$$

is found to equal -0.4713 a.u. or $-1.198\,D$ (C(+) − H(−)). The hydrogen forms the negative end of the dipole in spite of the relatively large value of 1.973 for the polarity factor λ/μ.

The method of density constraints as proposed and applied in this paper determines the molecular charge distribution entirely in terms of the expectation values of one-electron operators and one-electron integrals. The results obtained for methane demonstrate that such a method can yield a reliable representation of the molecular charge distribution. Because of the heavy weighting which the method of density constraints places on the valence charge distribution, this method could provide molecular charge distributions for SiH_4 and GeH_4 with an accuracy greater than that obtained from a regular SCF calculation. In fact the calculations for SiH_4 and GeH_4 by the present method represent no real increase in complexity over the CH_4 calculation since the increase in the number of orbitals in the cores on Si and Ge simply lead to an equivalent increase in the number of orthogonality restraints.

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