Potential functions of internal rotation and electric parameters of atoms of ethane molecules and its halogenated derivatives

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Based on the previously suggested approximate quantum mechanical description of potential functions of internal rotation and the calculation method, the regions of values of atomic charges and moments of ethane molecules and its halogenated derivatives have been found. They describe simultaneously experimental potential functions of internal rotation and dipole moments of molecules with an accuracy comparable to the experimental one. Potentials of internal rotation for some unstudied molecules of the series of halogenated derivatives of ethane have been predicted.

Key words: approximate quantum mechanical description, potential functions of internal rotation, dipole moments, ethane and its halogenated derivatives.

The correlations that relate coefficients in the Fourier-series expansion of the potential function of internal rotation to quantities characterizing the electric charge distribution in a molecule have previously been obtained[1—8] from the quantum mechanical expression of the electronic energy of molecules. In particular, the even potential function of internal rotation of a molecule with one rotating top (only such potential functions will be considered in further discussions) can be presented in the form:

$$V(\varphi) = \sum_{(\alpha,\beta)} \frac{1}{2} \left\{ \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} + \int_{V_\alpha} \frac{Z_\beta \rho_e \,\mathrm{d}\tau_1}{r_{1\beta}} + \int_{V_\beta} \frac{Z_\alpha \rho_e \,\mathrm{d}\tau_2}{r_{2\alpha}} + \int_{V_\alpha}\int_{V_\beta} \frac{\rho_{12}\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2}{r_{12}} \right\} = \frac{1}{2}\sum_l \left[\sum_{(\alpha,\beta)} V_{\alpha\beta l}\right](1-\cos l\varphi) = \frac{1}{2}\sum_l V_l\,(1-\cos l\varphi). \tag{1}$$

Here φ is the internal rotation angle (*i.e.*, the angle of the turn of one part of the molecule relative to another part); Z_α and Z_β are the charges of atomic nuclei with numbers α and β; V_α and V_β are the volumes of these atoms; $\mathrm{d}\tau_1$ and $\mathrm{d}\tau_2$ are the volume elements; $r_{\alpha\beta}$, $r_{1\beta}$, $r_{2\alpha}$, and r_{12} are the distances between the corresponding nuclei and the volume elements; ρ_e is the electron density; and ρ_{12} is the two-particle probability density. The $V_{\alpha\beta l}$ values can be expressed as

$$V_{\alpha\beta l} = -\left\{ Z_\alpha Z_\beta a_{\alpha\beta l} + \int_{V_\alpha} Z_\beta \rho_e a_{1\beta l}\,\mathrm{d}\tau_1 + \int_{V_\beta} Z_\alpha \rho_e a_{2\alpha l}\,\mathrm{d}\tau_2 + \int_{V_\alpha}\int_{V_\beta} \rho_{12} a_{12l}\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \right\}, \tag{2}$$

where $a_{\alpha\beta l}$, $a_{1\beta l}$, $a_{2\alpha l}$, and a_{12l} are the coefficients of the Fourier-series expansion of the reverse distances $1/r_{\alpha\beta}$, $1/r_{1\beta}$, $1/r_{2\alpha}$, and $1/r_{12}$, respectively. These coefficients depend only on geometric parameters of the conformer accepted as the beginning of reference of energy and internal rotation angles.

In the rougher approximation,[7—8] when $1/r_{1\beta}$, $1/r_{2\alpha}$, and $1/r_{12}$ have been expanded in the Taylor series in $r_{\alpha 1}$ and $r_{\beta 2}$ powers, the $1/r_{\alpha\beta}$ value has been expanded in the Fourier series, and in the expression of the two-particle probability density

$$\rho_{12}(1,2) = \rho_e(1)\rho_e(2) + \Delta\rho_{12}(1,2) \tag{3}$$

it is assumed that

$$\Delta\rho_{12}(1,2) = 0, \tag{4}$$

electric charges and atomic moments in molecules appear in Eq. (2) instead of integrals. For atoms with the number α we considered[7—8]

$$\text{the charge}\quad e_\alpha = Z_\alpha + \int_{V_\alpha} \rho_e \mathrm{d}\tau_1, \tag{5}$$

$$\text{the dipole moment}\quad \bar{\mu}_\alpha = \int_{V_\alpha} \rho_e \bar{r}_{\alpha 1}\,\mathrm{d}\tau_1, \tag{6}$$

and tensor elements of the quadrupole moment

$$Q^\alpha_{fg} = \int_{V_\alpha} \rho_e (3 f_{\alpha 1} g_{\alpha 1} - \delta_{fg} r^2_{\alpha 1})\,\mathrm{d}\tau_1, \tag{7}$$

where f, g = X, Y, Z, and δ_{fg} is the Kronecker delta.

The dipole moment and the elements of the atomic quadrupole moment are determined in the local system of coordinates, which originates from the atomic nucleus.

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Then it can be taken that atoms or atomic pairs of one type[9—11] in different molecules have approximately equal values of integrals (2) or, in the rougher approximation, equal values of atomic charges and moments. Then for several molecules consisting of atoms of different types, the values of integrals (2) or atomic charges (5) and moments ((6), (7)) can be, in principle, found by the known potential functions of internal rotation determined from experimental data or by the quantum mechanical calculation. After this, the calculated values of integrals (2) or charges (5) and moments ((6), (7)) can be used for determining potential functions of internal rotation of so far unstudied molecules consisting of atoms of the same types.

It is substantial to estimate the accuracy of the description of the charge distribution in molecules in terms of the approach presented. The values of integrals (2) or atomic charges (5) and moments ((6), (7)) calculated from potential functions are effective quantities due to the approximate character of the theory and the methods for determining potentials of internal rotation and to the assumption that atoms and groups of atoms of one type are equivalent in different molecules. Therefore, it is possible that the values determined by this method will not correspond to the real electric charge distribution in molecules. Nevertheless, the approach presented is based on the rigorous quantum mechanical theory and is the consistent, although approximate, application of the rigorous theory for establishing the correlation between the electric charge distribution in a molecule and parameters of the potential function of internal rotation. Therefore, one can expect that the found values of integrals (2) or atomic charges (5) and moments ((6), (7)) describe correctly at least the relative electric charge distribution in a molecule, which provides the possibility, in principle, to predict other properties of molecules depending on this distribution.

To check this possibility, relationships that relate charges (5) and dipole moments (6) of atoms to dipole moments of molecules have been obtained.[12] Then the values of charges (5) and moments ((6), (7)) of atoms in molecules of ethane and its simplest halogenated derivatives have been calculated[13] from the experimental dipole moments of these molecules and the V_l parameters of potential functions of internal rotation (1) found from the experimental data. The results obtained were considered to be preliminary,[13] and the calculation procedure needed more detailed studies. In addition, some new experimental data on potential functions of internal rotation of molecules of halogenated ethane derivatives have appeared recently. Therefore, the values of charges and dipole moments of atoms in mentioned molecules have been calculated additionally.

All experimental potential functions of internal rotation of molecules used in calculations refer to the gaseous phase,* and their parameters are presented in Tables 1—3. The values of parameters V_3 and V_6 calculated for all molecules except ethane from the experimental data by the method suggested by Lewis and coworkers[40] are presented in Table 1. It can be seen from Table 1 that the V_6 values are very small and, in addition, our calculations show that the V_3 values calculated with and without taking into account the coefficient V_6 agree within several percent (the maximum deviation of ~10 % is observed for CF_3CH_2Cl, CF_3CH_2Br, and CF_3CF_2Br). Therefore, only coefficients V_3 are used for calculating charges and moments of atoms.

The values of V_3 in the molecules, for which there is no sufficient experimental data for determining V_3 and V_6, are presented in Table 2. Our estimations of errors of determination of coefficients V_3 from experimental data are also presented in Tables 1 and 2.

Table 1. Values of parameters V_3 and V_6 of potential functions of internal rotation of ethane molecules and its halogenated derivatives with C_{3v} symmetry tops calculated from literature data (kJ mol^{-1})

Molecule	V_3^{exp}	V_6^{exp}	Estimation of experimental error V_3 (%)	Reference
$CH_3—CH_3$	12.06[a]	0.13[a]	10	15
$CH_2F—CH_3$	13.92	−0.06	10	16, 17
$CF_3—CH_3$	12.48	−0.09	10	18, 19
$CF_3—CH_2F$	14.79	−0.17	10	20, 21
$CH_2Cl—CH_3$	15.61	−0.07	10	17, 22
$CHCl_2—CH_3$	18.91	−0.26	15	23[b]
$CCl_3—CH_3$	23.48	−0.27	10	23, 24
$CH_2Br—CH_3$	15.61	−0.06	10	17, 25
$CHBr_2—CH_3$	17.32	0.03	15	23[b]
$CBr_3—CH_3$	23.97	0.07	15	23[b]
$CH_2Cl—CF_3$	17.66	0.59	15	20[b]
$CH_2Br—CF_3$	18.13	0.30	15	20[b]
$CFCl_2—CH_3$	18.50	−0.11	10	23, 26, 27
$CClBr_2—CH_3$	23.74	0.04	15	23[b]
$CF_2Br—CF_3$	19.50	0.92	15	28[b]

[a] The values of parameters V_3 and V_6 are taken from Ref. 15.
[b] The following accepted geometric parameters are used: r_{CC} = 1.52 Å, r_{CH} = 1.09 Å, r_{CF} = 1.35 Å, r_{CCl} = 1.77 Å, r_{CBr} = 1.93 Å, ∠CCR = 110° (R = H, F, Cl, and Br).

Table 2. Values of parameters V_3 of potential functions of internal rotation of halogenated ethane derivatives with C_{3v} symmetry tops (kJ mol^{-1})

Molecule	V_3^{exp}	Estimation of experimental error (%)	Reference
$CHF_2—CH_3$	13.39	15	29
$CF_3—CHF_2$	14.69	20	30
$CF_3—CF_3$	16.40	20	31
$CCl_3—CH_2Cl$	36.50	20	32
$CCl_3—CHCl_2$	52.31	25	14
$CCl_3—CCl_3$	63.61	25	32
$CF_2Cl—CH_3$	18.42	20	33
$CF_2Br—CH_3$	21.20	15	23
$CF_2Cl—CF_3$	21.34	20	34

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* See also the review and the critical analysis of the experimental potential functions of internal rotation of ethane molecules and its halogenated derivatives (Ref. 14).

Table 3. Values of parameters V_l and extreme values of potential functions of internal rotation (1) for 1,2-dihalogenated ethane derivatives (V_l /kJ mol^{-1}, φ/deg)[a]

Molecule	V_1	V_2	V_3	φ'[b]	$V_{max} = V_{(\varphi=\varphi')}$	φ_{gauche}	$V_{(\varphi=\varphi_{gauche})}$	$V_{(\varphi=180°)}$	Reference
CH_2F-CH_2F	8.14	−11.18	14.63	53.6	8.84	108.9	−3.40	22.77	35
CH_2F-CH_2Cl	7.27	−3.55	21.14	58.5	21.72	111.9	3.37	28.38	36, 38
CH_2F-CH_2Br	8.11	−3.74	16.12	59.0	16.45	112.2	4.24	25.23	37, 38
CH_2Cl-CH_2Cl[c]						107.7	4.60		39
CH_2Br-CH_2Br[c]						107.0	7.57		39
CH_2Cl-CH_2Br[c]						108.6	5.59		39

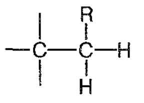
[a] It is accepted that $\varphi_{trans} = 0$ and $V_{(\varphi_{trans}=0)} = 0$. [b] φ' are the angles φ corresponding to the potential barrier of the *trans—gauche*-transition.

[c] The values of dihedral angles of *gauche*-conformers and differences in energies of conformers are taken from Ref. 39, and the parameters V_1—V_3 presented for other molecules are calculated in this work.

The errors are accepted to be minimum for the molecules, for which the experimental data (the values of torsion energy levels found by vibrational spectroscopy) make it possible to calculate coefficients V_3 and V_6 and for which geometric parameters have been determined experimentally. Maximum errors are ascribed to the molecules, for which the values of torsion frequencies in the gaseous phase have been estimated on the basis of the corresponding data obtained for the liquid phase. It is noteworthy that the values presented in Tables 1 and 2 reflect relative errors rather than absolute ones. The determination of absolute errors is considerably more difficult.

Table 3 presents extreme values of potential functions of internal rotation for molecules of 1,2-dihalogenated ethanes found from the experimental data (the potential barriers of *trans—gauche*-transitions, the differences in energies of conformers, and the potential barriers of *gauche—gauche*-transitions) and parameters V_1—V_3 calculated from experimental data. It is noteworthy that for the upper three molecules in Table 3 parameters V_1—V_4 and V_6 of series (1) have been determined previously (the references are given in Table 3); however, these calculations are performed taking into account deformations of tops in internal rotation (nonempirical quantum mechanical calculations have been performed with this purpose). Since in this work we use the model of a molecule with rigid rotating tops, the values of parameters V_1—V_4 and V_6 are recalculated by the method presented in Ref. 40. We use only parameters V_1—V_3 for further calculations, because parameters V_4 and V_6 are small and can be calculated only with great errors.

According to the structural formulas, the molecules considered contain "terminal" atoms of four types:[9—11] $R{-}C{<}$, where R = H, F, Cl, and Br, and "central" carbon atoms of fourteen types. However, charges of "central" atoms do not enter the formulas,[7] which relate coefficients V_l to values of charges and moments of atoms, and moments of these atoms enter only expressions for V_1 and V_2. Only molecules of 1,2-dihalogenated derivatives of ethane of all considered molecules have nonzero coefficients V_1 and V_2 (Table 3). Therefore, it is impossible to obtain values of charges and moments of "central" atoms for molecules with the C_{3v} top symmetry from Tables 1 and 2 for which $V_1 = V_2 = 0$, and there is no sense to classify the corresponding "central" atoms. Therefore, three types of "central" atoms



$$-\overset{|}{\underset{|}{C}}-\overset{R}{\underset{H}{C}}-H\ ,$$

where R = F, Cl, and Br, will be distinguished in further discussions.

The theory[7] allows one to calculate charges e_α(5), dipole moments μ_α(6), and quadrupole moments $Q^\alpha{}_{ZZ}$(7)* for "terminal" atoms, and for "central" atoms components of dipole $\mu^\perp{}_{CR}$ and quadrupole $Q^{C_R}_{XZ}$ and $(Q^{C_R}_{XX} - Q^{C_R}_{YY})$ moments** can be determined.

It has been indicated above that experimental values of dipole moments of molecules are also used in the calculation. Since for "central" atoms the theory[7] allows one to determine only components of dipole moments $\mu^\perp{}_{CR}$ perpendicular to the axis of internal rotation, only the value of projection of the dipole moment of a molecule on the plane perpendicular to the axis of internal rotation can be used for calculation (and then can be predicted).*** These projections are equal to zero

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* The axis symmetry of the electron density distribution relative to OZ axes, which connect nuclei of "terminal" and corresponding "central" atoms, is approximately accepted for "terminal" atoms.[7] Therefore, the dipole moments μ_α are directed along these axes, while the quadrupole moments of "terminal" atoms can be expressed by the elements $Q^\alpha{}_{ZZ}$.

** The following orientation of local systems of coordinates is accepted for "central" atoms: the OZ axis is directed toward the adjacent "central" atom, the OX axis lies in the plane of the CCR fragment, where R = F, Cl, and Br, and is directed toward the halogen atom, the OY axis is perpendicular to the CCR plane,[7] $\mu^\perp{}_{CR}$ is the projection of the dipole moment of the "central" atom on the plane perpendicular to the axis of internal rotation.

*** This restriction is removed if there are two or more axes of internal rotation in a molecule, so that atoms that are "central" for one axis are not "central" for another axis.

Table 4. Experimental values of dipole moments μ(D) of some substituted ethane derivatives (microwave data) and the components of dipole moments $\mu^{\perp}{}_{CH_2R}$ that are perpendicular to the axis of internal rotation and fall on the CH_2R group (R = F, Cl, and Br) calculated from these data

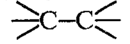
Molecule		μ	$\mu^{\perp}{}_{CH_2R}$
$CH_2F—CH_3$[41]		1.96±0.03	1.76
$CH_2F—CH_2F$[42]		2.67±0.09	1.64
$CF_3—CHF_2$[21]		1.80±0.22	1.70
$C_2H_5—CH_2F$	*trans*[43]	2.050±0.043	1.70
	gauche	1.902±0.064	
$C_2H_5—CH_2Cl$	*trans*[44]	1.95±0.06	1.72
	gauche	2.02±0.11	
$CH_3—CH_2Br$[45]		2.04±0.02	1.83

for molecules, whose both tops have the C_{3v} symmetry. Therefore, the values of dipole moments of less symmetric molecules are used in the calculation: CH_3CH_2F, CH_2FCH_2F (*gauche*), CF_3CH_2F, and CH_3CH_2Br. These values found from the analysis of microwave spectra, the calculated values of $\mu^{\perp}{}_{CH_2R}$, and the components of dipole moments of these molecules, which are perpendicular to axes of internal rotation and fall on the CH_2R (R = F, Br) group, are presented in Table 4. The value of $\mu^{\perp}{}_{CH2F}$ found from the microwave values of dipole moments of *trans*- and *gauche*-conformers of 1-fluoropropane (Table 4) agrees well with these data. Therefore, we include the value of $\mu^{\perp}{}_{CH_2Cl}$ (Table 4) found from the microwave values of dipole moments of *trans*- and *gauche*-conformers of 1-chloropropane in the calculation.

A specific feature of calculations, which appears due to the high symmetry of molecules of the series of substituted ethane derivatives, should be mentioned. Moments that are higher than quadrupole moments are not taken into account for atoms in molecules (otherwise the number of parameters determined would be too great), while for molecules with at least one symmetry (C_{3v}) top the coefficients V_l (l = 3, 6,...) are described only by interactions of "terminal" atoms. Since the values of charges and moments of atoms are calculated from the V_l values found from experimental data (and therefore, coefficients V_3, V_6, *etc.* also efficiently take into account the interactions of "central—central" and "central—terminal" pairs of atoms), the energies of interactions of "terminal" atoms are overestimated, and hence, the absolute values of charges and moments of "terminal" atoms are increased. This can make comparing them to the corresponding data obtained by other calculation methods, first, by the nonempirical quantum mechanical method in terms of the Bader method of division of molecules into atoms, difficult.[46]

The electron density distribution in the volumes of "central" carbon atoms entering the CR_3 tops (R = H, F, Cl, and Br) should have the C_{3v} symmetry. The electron density distribution in the volumes of "central" carbon atoms entering the CH_2R tops (R = F, Cl, and Br) has the C_s symmetry, but can be presented as the "perturbation" of the electron density of the C_{3v} symmetry (for the carbon atom, which enters the CH_3 top) due to the effect of a halogen atom (F, Cl, or Br).* Therefore, for all molecules in some variants of the calculation we present the V_3 coefficient in Eq. (1) as the sum

$$V_3 = V_3' + V_3^0, \tag{8}$$

where the V_3' coefficient reflects the interaction of pairs of "terminal" atoms and V_3^0 reflects the interactions of the "central—central" and "central—terminal" pairs of atoms. Then taking into account that all molecules considered have the common "central" fragment , we assume in the first approximation that parameters V_3^0 are constant for all molecules. The empirical parameter V_3^0 is determined from the experimental values of V_l along with charges and moments of atoms.

When coefficients V_3 are divided into components (8), the possibility appears to take into account the value of $\Delta\rho_{12}(1,2)$ in the form of the expression**

$$\int\limits_{V_{C_R}}\int\limits_{V_{C_{R'}}} \frac{\Delta\rho_{12}\,d\tau_1\,d\tau_2}{r_{12}} = \frac{1}{2}\sum_l \Delta V_{C_RC_{R'}\,l}(1-\cos l\varphi) \approx$$
$$\approx \frac{1}{2}\Delta V_{C_RC_{R'}\,3}(1-\cos 3\varphi).$$

instead of using condition (4) for central atoms.

In this case, the values of $\Delta V_{C_RC_{R'}3}$ (which in the first approximation can be assumed to be equal for all considered pairs of "central" atoms) enter the parameter V_3^0.

Using all data from Tables 1 and 2 and three upper lines of Table 3, 33 equations with V_l in the right part can be written. Using the data of Table 3, 12 equations with combinations of V_l in the right part can be written: six expressions of the $V'(\varphi_{gauche}) = 0$ type and six expressions of the $V(\varphi_{gauche}) \approx \Delta E$ type, where ΔE is the difference in energies of conformers. All these 45 equations are second-power equations, which comprise linear combinations of pair products of unknowns. Three linear equations, which relate charges and dipole moments of atoms to $\mu^{\perp}{}_{CH_2R}$ values[12] (R = F, Cl, and Br, see Table 4), can also be written. Thus, the maximum number of equations that can be written on the basis of the experimental data is 48. These equations contain 22 unknowns: the charges e_α, the dipole μ_α and quadrupole

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* In the latter case, the "deviation" of the electron density distribution from C_{3v} symmetry is taken into account in our approach, because nonzero moments of "central" atoms $\mu^{\perp}{}_{CR}$ and Q^{CR}_{XZ}, which enter only the equations with V_1, and $(Q^{CR}_{XX} - Q^{CR}_{YY})$, which enter only the equations with V_2 (here R = F, Cl, and Br), appear.

** The account for the $\Delta\rho_{12}$ value is the most important precisely for "central" atoms.[47]

$Q^{\alpha}{}_{ZZ}$ moments for "terminal" atoms of four types (α = H, F, Cl, and Br), the moments $\mu^{\perp}{}_{C_R}$, $Q_{XZ}^{C_R}$ and $(Q_{XX}^{C_R} - Q_{YY}^{C_R})$ for "central" atoms of three types (R = F, Cl, and Br), and the parameter $V_3{}^0$.

There are several algorithms, which allow one to solve systems of nonlinear equations, for example, the previously used Levenberg—Marquardt—Morrison algorithm[13] suggested by Osborn.[48] All these algorithms require specifying initial approximations for values determined and allow one, in the best case, to obtain the solution, which is the closest to the initial approximation. Thus, the choice of initial approximations for values determined is a very responsible procedure. Therefore, in this work we are not restricted by the choice of one or several similar initial approximations, as it has been done previously,[13] but we have estimated beforehand the regions of possible values of charges and moments of atoms and then refine them, solving the system of equations mentioned by exhaustion of all possible values of charges and moments of atoms (from the regions estimated beforehand). Since we assume that the calculated values of charges and moments of atoms can differ from the values corresponding to the real electric charge distribution in a molecule, wider regions of possible values compared to estimations based on physical considerations are considered for them.

For the parameter $V_3{}^0$, we consider the values to be equal to

$$V_3^0 = k \cdot V_3^{C_2H_6}, \qquad (9)$$

where $V_3^{C_2H_6}$ is the value of the potential barrier of internal rotation of an ethane molecule (Table 1), and k = 0, 0.5, 0.9, and 1.0.

For charges of hydrogen and halogen atoms, we consider the regions of values from +0.1 to −1.0 |e| and from 0.0 to −2.0 |e|, respectively, where |e| is the absolute value of the charge of an electron.

Since the axis symmetry relative to the axis connecting nuclei of "terminal" and "central" atoms[7] is assumed for the electron density (ρ_e) distribution in volumes of "terminal" atoms and also taking into account: (a) the determination of dipole (6) and quadrupole (7) moments of atoms, (b) the fact that $\rho_e < 0$, and (c) the chosen positive direction of dipole moments of "terminal" atoms (opposite to the direction of the vector $\bar{r}_{\alpha l}$ in Eq. (6)[7]), it can be expected that dipole and quadrupole moments of "terminal" atoms have positive and negative values, respectively. We consider the regions of values from 0.0 to ~10 D for dipole moments of hydrogen and halogen atoms, and for quadrupole moments of these atoms we consider the regions of values from 0 to $-10 \cdot 10^{-26}$ SGSE units and from 0 to $-45 \cdot 10^{-26}$ SGSE units, respectively.

Then the values of charges and moments of "terminal" atoms are selected, which reproduce the experimental values V_3 (Tables 1 and 2) within $\pm K \cdot \delta$, where δ are the estimations of the experimental errors of determination of coefficients V_3 presented in Tables 1 and 2 and the coefficient K takes the values from 1.0 to 1.5 with the interval of 0.1. The selected values of charges and moments of "terminal" atoms are used then for calculating the $\mu^{\perp}{}_{C_R}$ values of "central" atoms by the linear equations with $\mu^{\perp}{}_{CH_2R}$ (R = F, Cl, and Br).

The values of $Q_{XZ}^{C_R}$ and $(Q_{XX}^{C_R} - Q_{YY}^{C_R})$ (R = F, Cl, and Br) are calculated in the following way. First, the system of four nonlinear equations written for 1,2-dichloroethane and 1,2-dibromoethane (two equations with V_1 and V_2 for each molecule) is solved by the Levenberg—Marquardt—Morrison algorithm, and the values close to zero are accepted as initial approximations for values determined. Then only values, which reproduce the experimental values of $V(\varphi_{gauche}) = 0$ and $V(\varphi_{gauche}) \approx \Delta E$ for 1-chloro-2-bromoethane molecule with the accuracy not lower than $K \cdot (500\ \text{cm}^{-1})$ and $K \cdot (0.15 \cdot \Delta E)$, respectively, are selected from the solutions obtained. The obtained values of charges and moments of all "terminal" atoms and moments of "central" atoms C_{Cl} and C_{Br} allow one to calculate the values of $Q_{XZ}^{C_F}$ and $(Q_{XX}^{C_F} - Q_{YY}^{C_F})$ by the equations for V_1 and V_2 written, on the one hand, for molecules of 1-fluoro-2-bromoethane and, on the other hand, for 1-fluoro-2-chloroethane. The solutions, which give contradicting values of moments of the C_F atom, are rejected.

It should be mentioned that for 1,2-difluoroethane all solutions found give the values of V_3, which agree well with the experimental values (see Table 3), but none of these solutions reproduces, if only approximately, the experimental value of the difference in energies of conformers. All sets of charges and moments of atoms obtained predict that the energy of the *gauche*-conformer of this molecule is significantly higher than that of the *trans*-conformer, although it has been established experimentally that the *gauche*-conformer has a lower energy[49] (see Table 3).* It is likely that the correct description of the potential function of internal rotation of 1,2-difluoroethane is impossible in terms of the given simplified method for calculation.

The calculation procedure described results in sets of values of the charges and moments of atoms that reproduce the experimental values of parameters V_l with an accuracy comparable to experimental errors, and the experimental dipole moments of molecules are reproduced exactly. Table 5 presents some of these sets obtained for different coefficients k and K, which describe most exactly the experimental data. At k = 1.0 no solutions are found even for K = 1.5.

Analyzing the results of the calculations, some of which are presented in Table 5, it can be noted that for

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* The minimum calculated value of the difference in energies of *gauche—trans*-conformers is 5.83 kJ mol^{-1}.

Table 5. Electric parameters of atoms of ethane molecules and its halogenated derivatives calculated for different values of *k* and *K* (the charges are expressed in fractions of the absolute value of the charge of an electron, the dipole moments are expressed in D, and the quadrupole moments are expressed in 10^{-26} CGS units)

Parameter	Atom				Parameter	Atom		
	H	F	Cl	Br		C_F	C_{Cl}	C_{Br}
k = 0 (*i.e.*, the $V_3{}^0$ parameter was not introduced), *K* = 1.3								
e_α	−0.4	−0.6	−0.2	0.0	$\mu^{\perp}{}_{CR}$	0.77	1.20	2.04
μ_α	5	6	4	3	$Q^{C_R}_{XZ}$	1.75÷3.08	0.28÷0.50	0.86÷1.18
Q^{α}_{ZZ}	−2÷−1	−5	−22÷−19	−25÷−21	$Q^{C_R}_{XX} - Q^{C_R}_{YY}$	−0.20÷−0.01	−0.46÷−0.37	−0.25÷−0.18
k = 0 (*i.e.*, the $V_3{}^0$ parameter was not introduced), *K* = 1.4								
e_α	−0.4÷0.0	−1.2÷−0.4	−1.0÷−0.2	−0.8÷0.0	$\mu^{\perp}{}_{CR}$	0.77; 1.14 −2.71÷−0.17	0.46; 1.20 −4.53÷−0.35	0.20; 2.04 −4.00÷−0.65
μ_α	4÷5	3÷7	4÷8	3÷7	$Q^{C_R}_{XZ}$	−1.39÷5.22	−2.64÷0.75	−2.74÷1.64
Q^{α}_{ZZ}	−4÷−1	−11÷−4	−33÷−19	−39÷−20	$Q^{C_R}_{XX} - Q^{C_R}_{YY}$	−0.20÷0.33	−0.46÷0.00	−0.25÷0.00
k = 0.5, *K* = 1.1 (the first set of solutions)								
e_α	−0.2	−0.6	−0.8	−0.6	$\mu^{\perp}{}_{CR}$	−0.77	−1.59	−1.22
μ_α	3.5	4	6	5	$Q^{C_R}_{XZ}$	0.33÷0.69	0.28÷0.31	0.40
Q^{α}_{ZZ}	−1	−9	−29÷−26	−35	$Q^{C_R}_{XX} - Q^{C_R}_{YY}$	−0.07÷−0.03	−0.07÷−0.06	−0.02
k = 0.5, *K* = 1.1 (the second set of solutions)								
e_α	−0.5÷−0.4	−0.6	−0.4÷−0.2	−0.4÷−0.2	$\mu^{\perp}{}_{CR}$	0.77÷1.29	0.97÷1.71	0.77÷1.66
μ_α	4	5	3÷4	3÷4	$Q^{C_R}_{XZ}$	1.30÷4.28	0.36÷1.11	0.09÷1.38
Q^{α}_{ZZ}	−2÷−1	−6÷−5	−27÷−23	−31÷−25	$Q^{C_R}_{XX} - Q^{C_R}_{YY}$	−0.23÷−0.05	−0.35÷−0.19	−0.17÷−0.08
k =0.5, *K* = 1.2								
e_α	−0.5÷−0.2	−0.8÷−0.6	1.0÷−0.2	−1.0÷−0.2	$\mu^{\perp}{}_{CR}$	0.21÷1.71 −1.09÷−0.01	0.46÷1.72 −4.36÷−1.02	0.25÷1.66 −4.32÷−0.55
μ_α	3.5÷4.0	4÷5	3÷7	3÷6	$Q^{C_R}_{XZ}$	0.12÷5.60	−2.84÷1.11	−3.62÷1.39
Q^{α}_{ZZ}	−3÷−1	−9÷−5	−33÷−21	−39÷−23	$Q^{C_R}_{XX} - Q^{C_R}_{YY}$	−0.24÷0.25	−0.40÷0.15	−0.18÷0.10
k =0.9, *K* = 1.2								
e_α	−0.4	−0.6	−0.4	−0.4	$\mu^{\perp}{}_{CR}$	1.25	0.92	0.72
μ_α	2.5	4	3	3	$Q^{C_R}_{XZ}$	1.22÷5.60	1.01÷1.55	0.95÷1.37
Q^{α}_{ZZ}	0	−5÷−1	−28÷−27	−35÷−33	$Q^{C_R}_{XX} - Q^{C_R}_{YY}$	−0.11÷−0.02	−0.10÷−0.07	−0.03÷0.03

Note. Higher values of quadrupole moments correspond to lower values of charges or dipole moments in the regions presented, and *vice versa.*

values of charges and moments of atoms of ethane molecules and its halogenated derivatives there are the regions, which describe values of dipole moments of molecules and parameters V_l of the series (1) with the accuracy comparable to errors of determination of experimental data. The values of charges and moments of "terminal" atoms have reasonable (from the physical viewpoint) signs, although the absolute values of the charge of the hydrogen atom and of moments of atoms are strongly increased.* Introducing the parameter $V_3{}^0$ does not change the result. The moments of "central"

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* For example, the following values of atomic charges have been found for 1,2-difluoroethane and 1,2-dichloroethane molecules in Ref. 49 by nonempirical quantum mechanical calculation using the 6-31G* basis and the procedure of dividing molecules into atoms suggested by Bader:[46] ~0, −0.7, and −0.3|e| for hydrogen, fluorine, and chlorine, respectively.

Table 6. Calculated values of the V_3 parameters for the series of halogenated ethane derivatives (kJ mol^{-1})

Molecule	$V_3'+V_3^0 = V_3$	
	k = 0.5*, K = 1.1	k = 0.0 K = 1.3
CF_3—$CHCl_2$	23	27
CF_3—$CHBr_2$	23	26
CF_3—CCl_3	27	33
CF_3—CBr_3	27	30
CF_3—CCl_2Br	27	32
CF_3—$CClBr_2$	26	31
CF_3—$CFCl_2$	24	28
CF_3—$CFBr_2$	24	26
CF_3—$CClF_2$	21	23
CCl_2Br—CH_3	24	26
$CFBr_2$—CH_3	22	22
CCl_3—CH_2F	25	29
CCl_3—CHF_2	26	31
CCl_3—CF_2Br	50	42
CCl_3—CF_2Cl	44	45
CCl_3—$CFCl_2$	62	57
CBr_3—CH_2F	26	27
CBr_3—CHF_2	27	29

* The first set of solutions (see Table 5).

atoms have less determined values and differ even in sign in some variants of calculation; nevertheless, their values as a whole agree with one another in magnitude and sign within the given k and K.*

To elucidate stabilities of the calculated values of charges and moments of atoms relative to small changes in geometric parameters of molecules, we have performed the calculations, in which averaged geometric parameters are used for all molecules (see Note to Table 1), but this does not virtually change the results.

Using the solutions corresponding to $k = 0.5$, $K = 1.1$ (the first set of solutions) and $k = 0$, $K = 1.3$, the potential barriers of internal rotation V_3 have been calculated for some unstudied molecules of the series of halogenated ethane derivatives (Table 6). It is noteworthy that there are almost no experimentally studied molecules for which the potential function of internal rotation would be determined by the interactions of Br—Cl and Br—Br pairs of atoms (the data for 1-chloro-2-bromoethane and 1,2-dibromoethane are restricted, see Table 3). This results in the fact that different sets of charges and moments of atoms obtained for molecules with different interactions between atoms of the indicated type can predict noticeably divergent values of V_3 (they are not presented in Table 6). Refining these calculation data in terms of the approach described requires experimental studies of the CCl_3CBr_3, CBr_3CBr_3, *etc.* type molecules. The values of V_l calculated for 1,2-dihalogenated derivatives are not presented in Table 6, because these data for such molecules are also rather scarce (for example, it is desirable to study experimentally in detail 1,2-dichloroethane and 1,2-dibromoethane molecules).

Presently we have no sufficient grounds to choose one certain solution of those presented in Table 5 (the arguments in favor of the variants with lower k are insufficient, because they can result in loosing the physically significant solution). To do this (or at least to constrict regions of solutions), in the future we intend to take into account in calculations some other properties of molecules (for example, quadrupole moments and polarizabilities) and to calculate molecules of other classes.

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* In these calculations in the expression for the energy of the interaction of pairs of atoms, we take into account the terms containing products of quadrupole moments of pairs of "terminal" atoms. Neglecting these terms does not qualitatively change the results of calculations but results in higher absolute values of charges and moments.

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