

## **Floating spherical Gaussian orbital model study of average electric polarisabilities and magnetic susceptibilities : Some aliphatic hydrocarbons**

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**Abstract.** Floating spherical Gaussian orbital model is used to discuss the average electric polarisabilities and magnetic susceptibilities of a series of hydrocarbons. It has been noticed that the core contributions are negligibly small and these quantities (average electric polarisabilities and magnetic susceptibilities) can be well estimated from contributions localised on bond Gaussians.

**Keywords.** FSGO; polarisability; susceptibility.

### **1. Introduction**

Accurate calculations of molecular properties is one of the major aims of many models of the electronic structure of molecules. The floating spherical Gaussian orbital (FSGO) model proposed by Frost (1967) is quite attractive since the basis functions (i.e. Gaussians) are deployed intuitively according to the valence concepts of Lewis (1916) and Langmuir (1919) and the model predicts the electronic and geometric structures of singlet ground states of molecules with 'local' orbitals without the use of any arbitrary or semiempirical parameters. In this model each local orbital is classified as being either an inner-shell orbital, a bonding orbital or a lone-pair orbital. A certain degree of flexibility is introduced into the wave function by allowing the basis orbitals to float to positions of minimum energy by varying the exponents and positions of the basis orbitals. Blustin and Linnett (1974) have shown that the FSGO basis orbitals have good transferability between systems. In this paper we make use of the approximate transferability of core and bond Gaussians to approximate the wave functions of a series of aliphatic hydrocarbons and use symmetry-adapted double perturbation theory of Amos and Yoffe (1975) to estimate the average electric polarisabilities and magnetic susceptibilities of a series of systems.

## 2. Method of calculation

In the FSGO model the singlet ground state wavefunction is an antisymmetrised product of  $N$  floating spherical Gaussian orbitals, i.e.,

$$\Psi = A \theta_{00}, \quad (1)$$

where  $A$  is the antisymmetriser and

$$\theta_{00} = [\phi_1(1) \phi_1(2) \cdots \phi_N(2N-1) \phi_N(2N)] [\alpha(1) \beta(2) \cdots \alpha(2N-1) \beta(2N)], \quad (2)$$

$$\text{with } \phi_i(\alpha_i, R_{i,j}) = (2\alpha_i/\pi)^{3/4} \exp(-\alpha_i |r_j - R_i|^2). \quad (3)$$

The orbital exponents ( $\alpha_i$ ) and positions ( $R_i$ ) are chosen to minimise the variational energy

$$E = \langle \theta_{00} | AH | \theta_{00} \rangle / \langle \theta_{00} | A | \theta_{00} \rangle. \quad (4)$$

Since  $\phi_i$  satisfies the one-electron eigenvalue equation

$$h_i \phi_i = [-\frac{1}{2} \nabla^2 + 2\alpha_i^2 |r - R_i|^2] \phi_i = \epsilon_i \phi_i. \quad (5)$$

The product function  $\theta_{00}$  satisfies the following eigenvalue equation:

$$H_0 \theta_{00} = E_{00} \theta_{00}, \quad (6)$$

$$\text{where } E_{00} = 2 \sum_{i=1}^N \epsilon_i \quad \text{and} \quad H_0 = \sum_{i=1}^N h_i(2i) + h_i(2i-1)$$

using this  $H_0$  in conjunction with the symmetry-adapted double perturbation theory, Amos and Yoffe (1975) have shown that (in a.u.)

$$\bar{\alpha} = \frac{1}{2} \sum_{i=1}^N \frac{1}{\alpha_i^2} \quad \text{and} \quad \bar{\chi} = -\frac{1}{4} \sum_{i=1}^N \frac{1}{\alpha_i} \quad (7)$$

where  $\bar{\alpha}$  and  $\bar{\chi}$  are respectively the average electric polarisability and magnetic susceptibility of the  $2N$  electron system given by the FSGO model wavefunction  $\Psi$ . The expressions for  $\bar{\alpha}$  and  $\bar{\chi}$  show that these values depend only on the orbital exponents. FSGO model gives nearly the same values for orbital exponents in similar type of molecular structures. So in this paper we have used the standard values for orbital exponents (for C-C and C-H bonds) as given by Simons *et al* (1975) to approximate  $\Psi$  for the systems studied in this paper.

## 3. Results and discussion

The calculated average electric polarisabilities show good agreement with available experimental data. It may also be noted from table 1, the core Gaussian contributions to average electric polarisability is negligibly small as is expected. Calculated average magnetic susceptibilities for a series of aliphatic hydrocarbons are given in tables 2 and 3 along with available experimental data. Calculated values agree with experiment. The magnetic susceptibility values for saturated hydrocarbons are nearly 15% lower than the experimental results (see table 2) whereas

Table 1. Calculated average electric polarizabilities<sup>a</sup>.

System	$\bar{\alpha}_{\text{valance}}$	$\bar{\alpha}_{\text{core}}$	$\bar{\alpha}_{\text{total}}$	$\bar{\alpha}_{\text{exptl}}^b$
Methane	24.06	0.01	24.07	26.2
Butane	75.28	0.04	75.32	81.8
2,2-Dimethyl butane	110.81	0.05	110.86	118.8
2,2,3,3-Tetramethyl butane	146.34	0.07	146.41	153.1
Cyclohexane	101.25	0.05	101.30	109.8
Methyl cyclohexane	119.02	0.06	119.08	128.8
1,1-Dimethyl cyclohexane	136.78	0.07	136.85	146.7

<sup>a</sup> All quantities are in units of  $10^{-25}$  cm<sup>3</sup>.

<sup>b</sup> See Camail *et al* (1978) and references therein.

Table 2. Calculated magnetic susceptibilities<sup>a</sup> for saturated hydrocarbons.

System	$\bar{\chi}_{\text{core}}$	$\bar{\chi}_{\text{valance}}$	$\bar{\chi}_{\text{total}}$	$\bar{\chi}_{\text{exptl}}^b$
Methane	0.13	13.52	13.65	17.4
Ethane	0.26	23.50	23.76	26.8
Propane	0.39	33.32	33.71	38.6
Butane	0.52	43.14	43.66	50.3
<i>n</i> -Pentane	0.65	52.96	53.61	63.1
<i>n</i> -Hexane	0.78	62.78	63.56	74.3
<i>n</i> -Heptane	0.91	72.60	73.51	85.4
<i>n</i> -Octane	1.04	82.42	83.46	96.9
<i>n</i> -Nonane	1.17	92.24	93.41	108.1
<i>n</i> -Decane	1.30	102.06	103.36	119.5
<i>n</i> -Undecane	1.43	111.88	113.31	131.8
<i>n</i> -Hexadecane	2.08	160.98	163.06	187.5
2-Methyl propane	0.52	43.38	43.90	51.7
2,2-Dimethyl propane	0.65	53.44	54.09	63.1
2-Methyl butane	0.65	53.20	53.85	63.0
2,2-Dimethyl butane	0.78	63.26	64.04	76.2
2,2,3-Trimethyl butane	0.91	73.32	74.23	88.4
2-Methyl pentane	0.78	63.02	63.80	75.3
2,2-Dimethyl pentane	0.91	73.08	73.99	87.0
2,2,3-Trimethyl pentane	1.04	83.14	84.18	98.3
2-Methyl hexane	0.91	72.84	73.75	86.2
2,3-Dimethyl hexane	1.04	82.90	83.94	98.8
3-Methyl heptane	1.04	82.66	83.70	98.0
4-Methyl octane	1.17	92.48	93.65	109.6
4-Methyl nonane	1.30	102.30	103.60	121.4
2,6-Dimethyl octane	1.30	102.54	103.84	122.5
2,4-Dimethyl nonane	1.43	112.36	113.79	134.7
2,2,4,7,9,9-Hexamethyl decane	2.08	164.50	164.50	191.5

<sup>a</sup> All quantities are in  $-1 \times 10^{-6}$  c.g.s. units.

<sup>b</sup> Values obtained from Muly and Boudreaux (1976).

Table 3. Calculated magnetic susceptibilities<sup>a</sup> for unsaturated hydrocarbons.

System	$\bar{\chi}_{\text{core}}$	$\bar{\chi}_{\text{valence}}$	$\bar{\chi}_{\text{total}}$	$\bar{\chi}_{\text{exptl}}^b$
Propene	0.39	30.45	30.84	31.5
1-Butene	0.52	40.27	40.79	41.0
2-Butene	0.52	40.50	41.02	42.6
Isobutene	0.52	40.50	41.02	40.8
1-Hexene	0.78	59.91	60.69	66.7
1-Octene	1.04	79.55	80.59	89.5
2-Methyl 4-heptene	1.04	80.02	81.06	88.0
2,3-Dimethyl 1,3-butadiene	0.78	57.62	58.40	57.2
2,4-Dimethyl 2,4-hexadiene	1.04	77.72	78.76	78.7
Cyclohexene	0.78	56.28	57.06	57.5
1,3-Cyclohexadiene	0.78	53.76	54.54	48.6

<sup>a</sup> All quantities are in  $-1 \times 10^{-6}$  c.g.s. units.

<sup>b</sup> Same as in table 2.

for unsaturated hydrocarbons the calculated values are in much better agreement (see table 3) with experiment.

#### 4. Conclusion

We have made an attempt to describe a whole system in terms of its parts. This has been done by introducing the notion of transferability of bond and core Gaussians in the aliphatic hydrocarbons studied here. The observed additivity (Mulay and Boudreaux, 1976) of average electric polarisability and magnetic susceptibility in aliphatic hydrocarbons is consistent with the predictions of simple FSGO model. Since the core contributions are shown to be negligibly small these quantities can be fairly well estimated from the contributions localised on bond Gaussians.

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