

TABLE 4 — CALCULATED ELECTRON MOMENTUM DISTRIBUTIONS FOR BORON HYDRIDES

[Values in a. u.]

p	BH ₄ ⁻			B ₂ H ₆			B ₃ H ₈ ⁻			B ₄ H ₁₀		
	Bonds	C ⁺ + Bonds	Total	Bonds	2C+ Bonds	Total	Bonds	3C+ Bonds	Total	Bonds	4C+ Bonds	Total
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.2	1.044	1.048	1.050	1.282	1.290	1.290	2.996	1.008	2.004	2.319	2.335	2.328
0.4	3.962	3.978	3.973	4.878	4.910	4.897	7.453	7.501	7.476	8.819	8.883	8.846
0.6	7.459	7.495	7.463	9.552	9.624	9.566	14.652	14.760	14.673	17.890	18.035	17.922
0.8	9.275	9.337	9.277	12.837	12.961	12.843	19.952	20.138	19.963	24.993	25.241	25.023
1.0	8.274	8.368	8.303	12.682	12.870	12.724	19.602	19.884	19.667	24.683	25.059	24.784
1.2	5.518	5.649	5.605	9.475	9.737	9.618	14.085	14.478	14.312	17.395	17.919	17.688
1.4	2.829	3.000	2.984	5.472	5.814	5.754	7.577	8.090	8.019	8.947	9.631	9.505
1.6	1.141	1.354	1.357	2.501	2.927	2.918	3.171	3.810	3.811	3.489	4.341	4.310
1.8	0.371	0.626	0.637	0.921	1.441	1.459	1.086	1.851	1.884	1.090	2.110	2.134
2.0	0.099	0.396	0.408	0.290	0.884	0.910	0.320	1.211	1.248	0.290	1.478	1.519
3.0	0.0	0.447	0.457	0.0	0.894	0.919	0.0	1.341	1.376	0.0	1.788	1.839

(a) C is the the core contribution from BH₄⁻

for the systems studied. It seems from the present study that the 'core' contributions to EMD's and CP's are quite insensitive to the molecular environment and hence can be transferred from molecule to molecule.

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Use of Ab-initio Valence-electron Wavefunctions : Average Electric Polarizabilities & Magnetic Susceptibilities of Some Hydrocarbons

SHOBHA BHARGAVA & N. K. RAY*

Department of Chemistry, University of Delhi, Delhi 110 007

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Ab-initio valence-electron wavefunctions are used in conjunction with symmetry adapted double perturbation theory to estimate the average electric polarizabilities and magnetic susceptibilities of some hydrocarbons. The predicted results are in good agreement with available experimental data.

WE have recently shown¹ that ab-initio valence-electron wavefunctions of Topiol *et al.*² can be successfully used to estimate the average electric polarizabilities (α) and magnetic susceptibilities ($\bar{\chi}$) of methane, ethane, ethylene, acetylene and cyclopropane and the calculated results are very close to those obtained from all-electron standard

FSGO model³ wavefunctions. We have also successfully estimated⁴ the average electric polarizabilities and magnetic susceptibilities of a large number of hydrocarbons assuming approximate transferability of 'bond' and 'core' Gaussians in the all-electron FSGO model. Since the 'core' contributions are known to be negligibly small^{1,4}, an attempt has, therefore, been made in this note to estimate the above two physical properties using the ab-initio valence-electron wavefunctions of Topiol *et al.*² Here again we consider the transferability of bond Gaussians^{4,5} to construct the ab-initio valence-electron wavefunctions for larger hydrocarbon systems. These wavefunctions are used in conjunction with symmetry adapted double perturbation theory of Amos⁶ to derive general expressions for α and $\bar{\chi}$ for various hydrocarbons studied in this note. The derived expressions are given below :

Case I—Open chain saturated hydrocarbons (C_nH_{2n+2})

$$P_m = K_m \left[\frac{(n-1)}{\alpha_{C-C}^m} + \frac{(2n+2)}{\alpha_{C-H}^m} \right] \quad \dots(1)$$

Case II—Closed chain saturated hydrocarbons (C_nH_{2n})

$$P_m = K_m \left[\frac{n}{\alpha_{C-C}^m} + \frac{2n}{\alpha_{C-H}^m} \right] \quad \dots(2)$$

Case III—Open chain hydrocarbons with single double bond (C_nH_{2n})

$$P_m = K_m \left[\frac{2}{\alpha_{C=C}^m} + \frac{(n-2)}{\alpha_{C-C}^m} + \frac{ne}{\alpha_{C-H}^m} + \frac{(2n-ne)}{\alpha_{C-H}^m} \right] \quad \dots(3)$$

with $m = 1$, Eqs. (1), (2) and (3) describe the magnetic susceptibility ($\bar{\chi}$) for the three cases given above. With $m = 2$, these equations give the average electric polarizability (α). In the above expressions

TABLE 1 — CALCULATED AVERAGE ELECTRIC POLARIZABILITIES
[In units of 10^{-25}cm^3]

System	Average polarizability		
	Model potential	FSGO ^a	Exptl ^b
Butane	80.2	75.32	81.8
2,2-Dimethyl. butane	116.8	110.86	118.8
2,2,3,3-Tetramethylbutane	153.4	146.41	153.1
Cyclohexane	109.7	101.30	109.8
Methylcyclohexane	128.0	119.08	128.8
1,1-Dimethylcyclohexane	146.3	136.85	146.7

(a) Obtained from ref. 4; and (b) obtained from ref. 7.

TABLE 2 — CALCULATED MAGNETIC SUSCEPTIBILITIES

System	Magnetic susceptibility ($-1 \times 10^{-6}\text{egs}$)		
	Model potential	FSGO ^a	Exptl ^b
Methane	13.9	13.65	17.4
Ethane	24.2	23.76	26.8
Propane	34.4	33.71	38.6
Butane	44.6	43.66	50.3
<i>n</i> -Pentane	54.9	53.61	63.1
<i>n</i> -Hexane	65.1	63.56	74.3
<i>n</i> -Heptane	75.4	73.51	85.4
<i>n</i> -Octane	85.6	83.46	96.9
<i>n</i> -Nonane	95.8	93.41	108.1
<i>n</i> -Decane	106.1	103.36	119.5
<i>n</i> -Undecane	116.3	113.31	131.8
<i>n</i> -Hexadecane	167.5	163.06	187.5
Propene	31.1	30.84	31.5
1-Butene	41.3	40.79	41.0
2-Butene	41.6	41.02	42.6
1-Hexene	61.8	60.69	66.7
1-Octene	82.3	80.59	89.5
2-Methyl-4-heptene	82.6	81.06	88.0

(a) Taken from ref. 4; and (b) taken from ref. 8.

K_2 is 0.5 and K_1 is -0.25 , n_e is the number of ethylenic C-H bonds, α_{C-C} , $\alpha_{C=C}$, $\alpha_{C-H(\text{me})}$ and α_{C-H_e} are respectively the exponents of the Gaussians for the bonds C-C (single), C=C (double), C-H (methane) and C-H (ethylene). Values of these Gaussian exponents are taken from the work of Topiol *et al.*² and $\bar{\alpha}$ and $\bar{\chi}$ values are estimated using the equations given above. These calculated quantities are given in Tables 1 and 2 along with experimental results. The results obtained from all-electron FSGO wavefunctions are also listed for comparison. Considering the simplicity of the model used our results seem to be in excellent agreement with available experimental data^{7,8}.

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Inclusion of Polarization Functions in Molecular SCF Calculations

R. A. THURAISSINGHAM

Department of Chemistry, University of Colombo, Sri Lanka

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Molecular SCF calculations including polarization functions are reported for CH_4 , SiH_4 , $(\text{CH}_3)_3\text{N}$, $(\text{SiH}_3)_3\text{N}$ and SiH_6 . For molecules containing second row atoms the effect of inclusion of d functions in the basis set is more than just polarization of orbitals; these partake in bonding. The planar geometry of $(\text{SiH}_3)_3\text{N}$ is predicted only when the basis set includes d functions on the silicon atom.

IN an atom the potential field which determines the orbital shape has spherical symmetry. However as soon as the atom is a part of a molecule the effective field on its electrons is no longer spherical. The charge cloud will be perturbed or polarized into a nonspherical charge. The simplest way to express the polarization is by the addition of small amounts of p functions for s orbitals and d_σ and d_π functions for p_σ and p_π wavefunctions respectively. This could be done by including in the basis set of a self-consistent field (SCF) calculation, d functions on the first row atom and p functions on the hydrogen.

In the case of second row atoms which have low lying d orbitals the effect may be different, more than mere polarization. They could partake in bonding, in which case the coefficients of these d functions in the molecular orbitals can be quite high. These effects will be examined in the calculations reported in this note.

Near Hartree-Fock (HF) calculations on CH_4 and SiH_4 —The calculations in this section were made to find out the contribution of polarization functions (PF's) to the SCF energy and the effect they have when the central atom changes from a first row atom to a second row atom.

The calculations were made for the methane molecule using the tetrahedral geometry¹ with C-H = 2.066a.u.[†] with and without polarization functions (PF's). In the calculation without PF's the basis set used was: C (10 s , 6 $p/5$ s , 3 p) and H (5 $s/3$ s). The gaussian exponents of hydrogen contraction were scaled to fit a Slater type orbital (STO) of 1.2. The calculations including PF's used a basis set of C (10 s , 6 $p/5$ s , 3 p , 1 d)² and H (5 s , 1

†1 a.u. (atomic unit) of length = 5.292×10^{-11} m