

Electron momentum distributions and Compton profiles of some molecules with FSGO model

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Abstract. The electron momentum distributions and the Compton profiles (within the impulse approximation) of H_2 , LiH, methane, water, acetylene, ethylene, ethane cyclopropane and cyclobutane have been calculated using the floating spherical Gaussian orbital (FSGO) wavefunctions. The agreement of the single-FSGO Compton profiles with the corresponding experimental or the Hartree-Fock (HF-SCF) theoretical ones is fairly good in most of the cases examined. The advantages and drawbacks of using the FSGO model for the calculation of Compton profiles are discussed.

Keywords. Electron momentum distributions; Compton profiles; FSGO model of molecular structure.

1. Introduction

Recently there has been a revival of interest in the electron momentum distributions (EMD) and Compton profiles (CP) of molecules. (For review, see Epstein and Tanner 1976). In the present paper, we shall confine our attention to the theoretical calculation of CP's of some small molecules. The first calculation of the shape of the Compton line for H_2 was done by Hicks (1937) using valence-bond wavefunction of Weinbaum (1933). Duncanson and Coulson (1941) calculated CP's of methane, ethane, ethylene and acetylene. Epstein and Lipscomb (1970) presented a general algorithm for obtaining EMD's using HF-SCF wavefunctions of polyatomic molecules. This algorithm was applied to evaluate CP's of hydrocarbons using a localized molecular orbital (LMO) approach (Epstein 1970). Some more studies using LMO approach have been recently reported (Smith and Whangbo 1974) for a number of molecules including hydrocarbons. The CP of water has been calculated using a variety of wavefunctions and compared with recent experimental results (Tanner and Epstein 1974). The effect of hydrogen bonding on the CP of water has also been examined in detail (Whangbo *et al* 1974). Thus, with growing interest on the theoretical side and the use of

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LMO's the suggestion (Hicks 1940) that CP's of large molecules may be predicted from an analysis of smaller molecules seems to be coming true.

There has been of late an increased activity on the experimental side as well. X-ray Compton profile measurements have been carried out on H₂ (Eisenberger 1970). The CP of LiH has been studied in detail using x-rays as well as γ -rays. (Phillips and Weiss 1969; Felsteiner *et al* 1972; Paakari *et al* unpublished results quoted by Aikala *et al* 1976). CP's of a host of hydrocarbons have been measured using x-rays and electron scattering (Eisenberger and Marra 1971; Bennani *et al* 1976).

In this paper, we have studied the suitability of the floating spherical Gaussian orbital (FSGO) model of molecular structure (Frost 1967 *a*) in calculating the CP's of some molecules. FSGO's have not been used so far in the calculation of CP's. Being local in nature (Nelson and Frost 1973) the FSGO's are of interest since LMO's have already proved a success in the calculation of EMD's of several molecules. FSGO's have also been used in the synthesis of wavefunctions (Christoffersen 1972) of larger molecules from the corresponding fragments and thus offer a convenient way of obtaining the EMD's of larger systems. It is with these points in mind that we embarked on a program of testing the suitability of the FSGO's in calculating CP's.

2. FSGO model in the momentum space and CP calculations

In the FSGO model (Frost 1967 *a*) for a closed shell molecule, a floating Gaussian

$$\psi_i(\mathbf{r}) = (2a_i/\pi)^{3/2} \exp[-a_i \{(x - A_i)^2 + (y - B_i)^2 + (z - C_i)^2\}] \quad (1)$$

where a_i is the orbital exponent and A_i, B_i, C_i are the Cartesian coordinates of the orbital centre used for an electron pair. The energy is minimized by optimization of all nuclear coordinates, orbital exponents and some or all of the orbital centres. The use of only single spherical Gaussian orbital per electron pair limits the accuracy of this model. The energies obtained are typically 85% of the corresponding Hartree-Fock (HF) energies. However, the use of such restricted basis makes this model extremely simple. Due to floating of the orbital centres, the FSGO wavefunctions satisfy the virial theorem very closely. The wavefunctions correspond to the chemist's picture in terms of the bond pair, inner shell and lone pair. Hence, it was felt worthwhile to calculate CP's from these wavefunctions and compare the results with those obtained from the more accurate HF-SCF wavefunctions and experiment.

Following Epstein and Lipscomb (1970) we find that the momentum density $|\chi(\mathbf{p})|^2$ is

$$\sum_{j,k} \rho_{jk} f_j(p) f_k(p) Y_{l_j m_j}(\theta_p, \phi_p) Y_{l_k m_k}(\theta_p, \phi_p) \exp(-i\mathbf{p} \cdot \mathbf{r}_{jk}) \quad (2)$$

where ρ is the density matrix, $f_j(p)$ and $f_k(p)$ are the Fourier transforms of the radial part of the basis orbitals. As shown in the above work, $\exp(-i\mathbf{p} \cdot \mathbf{r}_{jk})$ can be expanded in terms of the spherical Bessel functions,

$$\exp(-i\mathbf{p} \cdot \mathbf{r}_{jk}) = 4\pi \sum_{l,m} (-i)^l j_l(pr_{jk}) Y_{lm}(\theta_p, \phi_p) Y_{lm}(\theta_{jk}, \phi_{jk}). \quad (3)$$

Since only *s*-type Gaussians are involved in the present model, the radial momentum density,

$$I(p) dp = \int |\chi(\mathbf{p})|^2 p^2 \sin \theta_p d\theta_p d\phi_p dp \quad (4)$$

can be written, apart from some numerical constants, as a sum of the terms of the form

$$\rho_{jk} f_j(p) f_k(p) j_0(pr_{jk}) p^2 \quad (5)$$

where

$$j_0(pr_{jk}) = \sin(pr_{jk})/(pr_{jk}) \quad (6)$$

ρ_{jk} is equal to $2T_{jk}$ where T_{jk} is the (*j*, *k*)-th element of the inverse overlap matrix. The Fourier transforms ($f_j(p)$ and $f_k(p)$ in eq. (5)) are also Gaussians, *e.g.*,

$$f_j(p) = (1/2\pi a_j)^{3/2} \exp(-p^2/4a_j). \quad (7)$$

The Compton profile, $J(q)$, within the impulse approximation (Platzman and Eisenberger 1970), can be obtained as

$$J(q) = \frac{1}{2} \int_{|q|}^{\infty} I(p) |p| dp \quad (8)$$

where q is the projection of the electron's initial momentum upon the scattering vector.

The integration in eq. 8 can be carried out numerically using Simpson's rule. Thus, due to the use of only *s*-type single Gaussian orbitals, CP can be obtained from the wavefunction with very little computer time. The total time taken for all the calculations presented here was about 6 min without any use of molecular symmetry, on IBM 7044 computer.

In the next section we present results of our calculations of CP's on some molecules. Comparison with other HF-SCF data as well as the experimental results wherever available, is also made.

3. Results and discussion

(a) *Hydrogen*: The CP of H_2 was calculated from FSGO wavefunction employing just one Gaussian, centred at the mid-point of the bond (Frost 1967 *b*). This wavefunction leads to an energy approximately equal to 85% of the HF-SCF energy for H_2 . The FSGO-theoretical profile along with the experimental one (Eisenberger 1970) and SCF-theoretical profile calculated from Liu's wavefunction (Brown and Smith 1972) is shown in figure 1. The FSGO-theoretical profile has a $J(0)$ value less than the experimental one by about 6%. It also dies off faster than the experimental profile in the higher q -region.

(b) *Lithium hydride*: $I(p)$ was calculated for the FSGO wavefunction (Frost 1967 *a*). This shows an interesting feature in that $I(p)$ for the molecule is very nearly equal to the sum of the individual-orbital contributions to $I(p)$. In other words, the curve is nearly identical to the solid line shown in figure 2 for the sum of the bond pair and inner shell contributions. There are two maxima in the curve in figure 2, corresponding to the maxima for the inner shell and the bond

orbital. The reason for this additivity is that the off-diagonal elements of the inverse overlap matrix T are small in this case. The CP calculated from this wavefunction along with the experimental profile (Paakari *et al* 1975, quoted by Aikala *et al* 1976) is shown in figure 3. Our FSGO theoretical $J(O)$ value is higher than the experimental one by about 10% and the width, $q_{0.5}$, of this

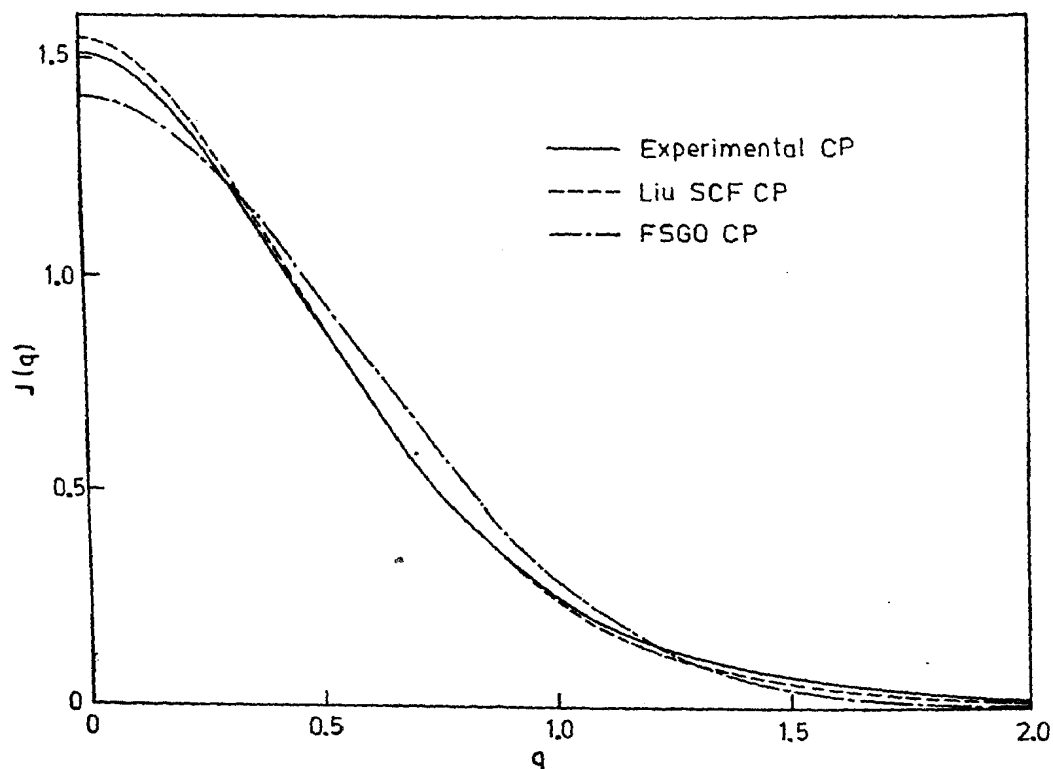


Figure 1. Compton profile of H_2 .

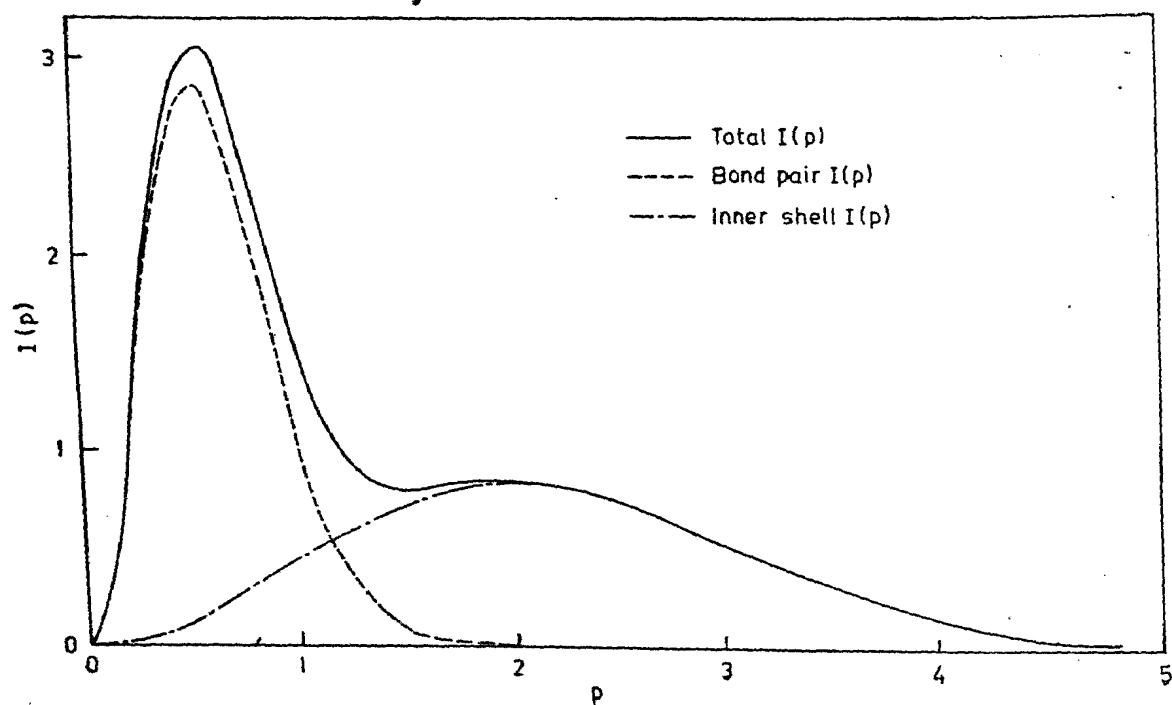


Figure 2. $I(p)$ for LiH.

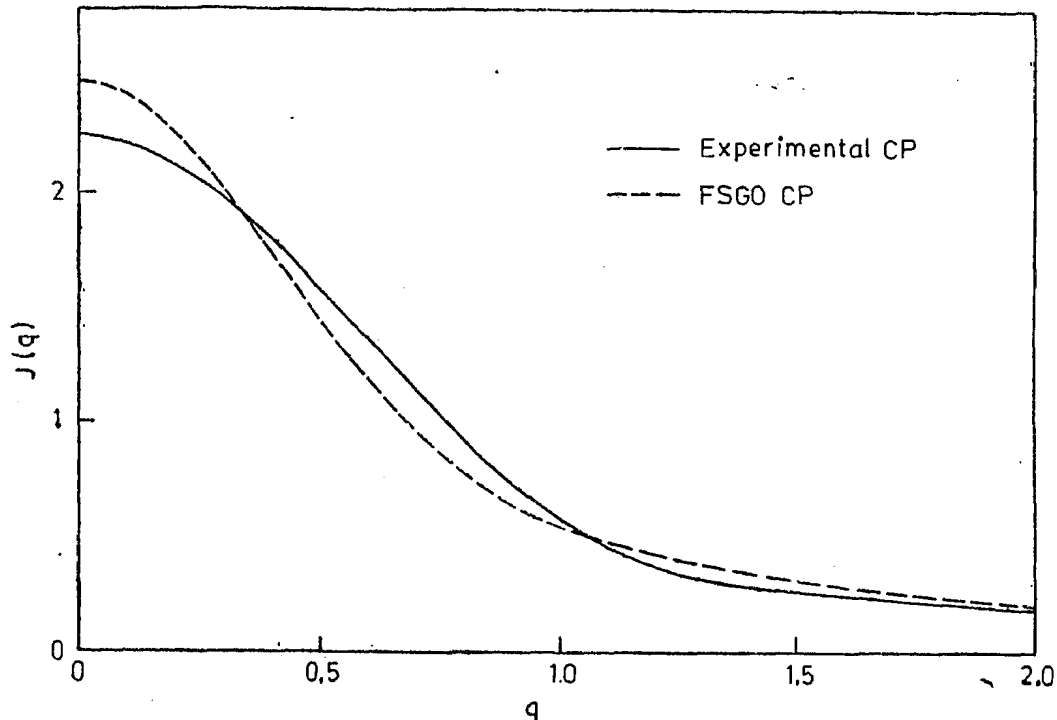


Figure 3. Compton profile of LiH.

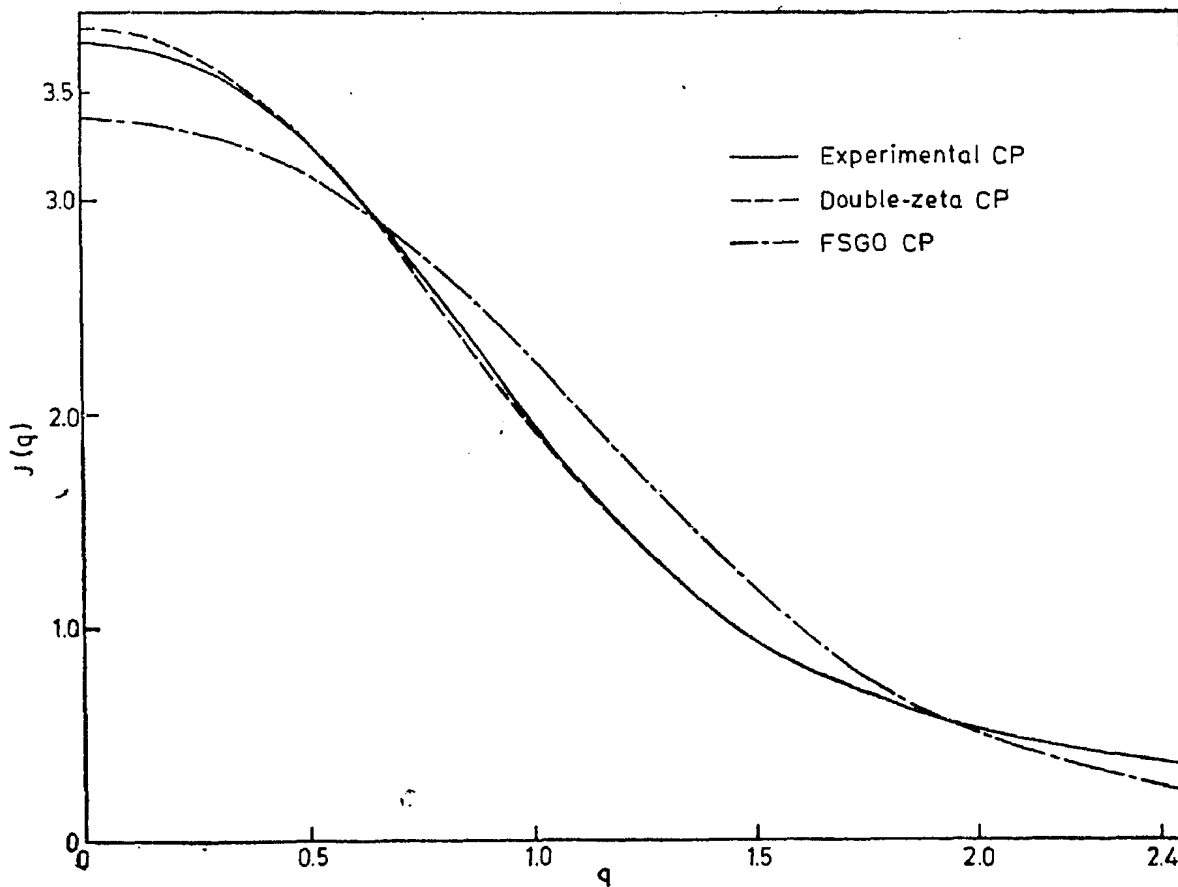


Figure 4. Compton profile of water.

profile, *i.e.*, the value of q at which $J(q) = \frac{1}{2} J(0)$ is lower than that for the experimental profile. This is a consequence of using a wavefunction of relatively poor energy in which the inner shell is not well-represented.

(c) *Water*: The FSGO-theoretical curve calculated from the wavefunction reported in the literature (Frost 1968), along with the experimental and double-

zeta-theoretical profile (Tanner and Epstein 1974) is presented in figure 4. In the higher q -region, the FSGO-CP dies off much faster than the experimental one. In this regard, the present results bear a similarity to those obtained earlier for the CP of water using minimal basis-set (Tanner and Epstein 1974).

(d) *Hydrocarbons*: All the calculations for hydrocarbons were done using the wavefunction available in the literature (Frost and Rouse 1968). In figure 5, the calculated $I(p)$ vs p for staggered ethane is shown along with the sum of the individual orbital $I(p)$'s. These two curves do not agree closely with each other. The reason for this discrepancy seems to be the numerically large values of the off-diagonal elements of the inverse overlap matrix T .

In table 1 we present our FSGO-CP results for methane, staggered ethane and acetylene along with the CP's calculated by adding the corresponding LMO contributions reported by least-squares fit to the experimental CP's of a host of molecules (Eisenberger and Marra 1971). In table 2, the CP data for ethylene, cyclopropane and cyclobutane are presented.

We have also calculated the CP for eclipsed ethane. This is very close to the profile of staggered ethane. Thus, within the FSGO-model-framework, it is not possible to distinguish between CP's of these two rotational isomers of ethane.

The agreement of the FSGO theoretical CP's with the corresponding experimental profiles, wherever available, is fairly good except for the higher q -region. This is obviously a consequence of using wavefunctions with poor energies in which the inner shell is not represented properly.

4. Conclusions

The FSGO-momentum distributions and CP's agree fairly well with the experimental results, except in the higher q -regions. The simplicity of the FSGO model

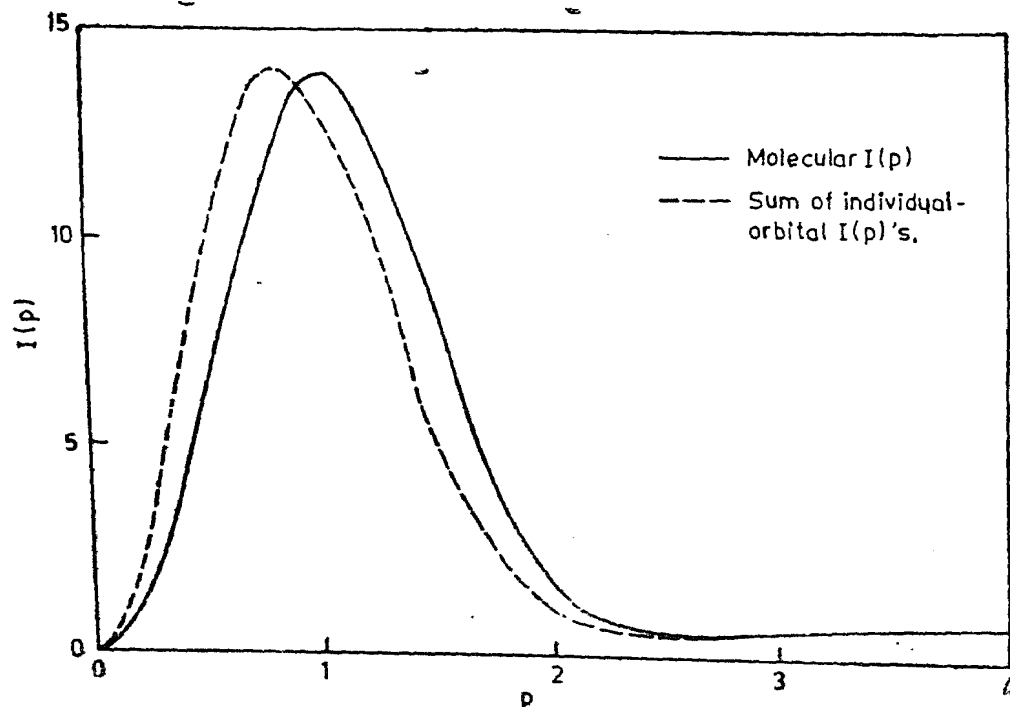


Figure 5. $I(p)$ for staggered ethane.

Table 1. Compton profiles^a of methane, ethane and acetylene

q	Methane		Ethane		Acetylene	
	FSGO Theory	Experimental ^b	FSGO Theory ^c	Experimental ^b	FSGO Theory	SCF ^d Theory
0.0	4.741	4.987	8.204	8.459	5.933	5.953
0.1	4.709	4.989	8.147	8.370	5.896	
0.2	4.612	4.770	7.976	8.128	5.787	
0.3	4.447	4.505	7.695	7.608	5.602	
0.4	4.216	4.174	7.307	7.213	5.341	
0.5	3.920	3.772	6.822	6.584	5.007	4.853
0.6	3.568	3.336	6.250	5.900	4.607	
0.7	3.173	2.892	5.611	5.189	4.154	
0.8	2.754	2.456	4.928	4.476	3.666	
0.9	2.332	2.051	4.228	3.800	3.166	
1.0	1.927	1.686	3.545	3.177	2.677	2.526
1.2	1.235	1.114	2.334	2.166	1.815	
1.4	0.750	0.765	1.449	1.498	1.188	
1.6	0.463	0.575	0.908	1.108	0.796	
1.8	0.316	0.473	0.625	0.889	0.586	
2.0	0.248	0.386	0.494	0.732	0.485	0.653

a. FSGO theoretical profiles normalised to the corresponding number of electrons in the range $0 \leq q \leq 20$. FSGO wavefunction (Frost and Rouse 1968) were used.

b. Constructed from the LMO fit of the experimental CP data (Eisenberger and Marra 1971)

c. CP for staggered ethane.

d. Calculated from the LMO profiles for $C \equiv C$ (Epstein and Tanner 1976)

is a very attractive feature. This is an *ab initio* model in which no empirical parameters are used. The orbitals used here can be interpreted in terms of the classical chemical pictures such as inner shell, bond pair and lone pair. Christoffersen has extended this model to "synthesise" larger molecules from the corresponding molecular fragments (for review see Christoffersen 1972). Hence, the calculations of EMD's and CP's of large molecules of chemical interest such as naphthalene, acetylcholine, etc., can be undertaken. However, the single-FSGO-model, used in the present work, has some drawbacks. As noted, earlier, the inner shell is not represented properly, leading to poorer energies. Since the long-range behaviour of CP is governed by the inner-shell, single-FSGO's lead to narrower CP. This behaviour can be improved in two ways. Use of a double-Gaussian, instead of single one, improves the energies markedly (Rouse and Frost 1969). Secondly, a model using two orbitals for the inner shell has also been reported (Ford *et al* 1970). Models incorporating a larger number of FSGO's

Table 2. Compton profiles^a of ethylene, cyclopropane and cyclobutane.

q	Ethylene		Cyclopropane		Cyclobutane	
	FSGO Theory	Experimental ^b	FSGO Theory	Experimental ^b	FSGO Theory	Experimental ^b
0.0	7.061	7.359	10.480	10.414	13.891	13.836
0.1	7.013	7.278	10.408	10.318	13.796	13.757
0.2	6.872	7.068	10.193	10.075	13.515	13.435
0.3	6.638	6.709	9.844	9.662	13.057	12.882
0.4	6.314	6.253	9.370	9.115	12.432	12.154
0.5	5.905	5.703	8.782	8.412	11.659	11.270
0.6	5.422	5.104	8.095	7.693	10.738	10.257
0.7	4.880	4.489	7.324	6.889	9.752	9.185
0.8	4.299	3.880	6.494	6.059	8.670	8.079
0.9	3.703	3.368	5.633	5.247	7.548	6.996
1.0	3.120	2.783	4.776	4.475	6.427	5.966
1.2	2.084	1.916	3.218	3.155	4.364	4.207
1.4	1.324	1.386	2.042	2.198	2.774	2.931
1.6	0.855	1.042	1.304	1.599	1.761	2.132
1.8	0.607	0.861	0.913	1.250	1.223	1.668
2.0	0.499	0.716	0.731	1.038	0.975	1.384

a. FSGO theoretical profiles normalised to the corresponding number of electrons in the range $0 \leq q \leq 20$ calculated from the wavefunction available in the literature (Frost and Rouse 1968).

b. Constructed from the LMO fit of the experimental CP data (Eisenberger and Marra 1971)

per electron pair have also been recently reported (Nelson and Frost, 1973; Karunakaran and Christoffersen, 1975). The EMD's and CP's calculated from these two types of wavefunctions are expected to be better than the present ones.

In the single-FSGO-model, the lone pair and π -bond orbital centres have to be constrained rather arbitrarily, since they tend to collapse into the nucleus (Frost 1968). The model, which employs two orbitals to represent π -bond and lone pair (Ford *et al* 1970) is therefore expected to give a better agreement with the experimental CP's of molecules having π -bonds or lone-pairs.

Since the present model is within the orbital-approximation electron correlation effects are not included. The importance of correlation on the EMD's and CP's has been stressed (Benesch and Smith 1970). In spite of these drawbacks the FSGO model offers a very simple way of theoretically calculating CP's for fairly large molecules.

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