Theoret. Chim. Acta (Berl.) 51, 97–106 (1979)

THEORETICA CHIMICA ACTA

Magnetic Susceptibilities of Acetylene and Ethylene Using Frost-Model Wavefunctions with *p*-Type Gaussians

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There are degeneracy problems involved in the calculation of magnetic susceptibilities from Frost model wavefunctions built up from mixed *s*- and *p*-type Gaussians. Various methods are suggested to alleviate the difficulties and they are used to compute the susceptibilities of C_2H_2 and C_2H_4.

Key words: Magnetic susceptibilities – Frost model – *p*-type Gaussians

1. Introduction

The Frost model [1] ground-state wavefunction using a Lewis basis set, that is one orbital per electron pair, is the antisymmetrized product of n doubly occupied floating Gaussian orbitals. Thus we can write the zero order function as $\mathscr{A}\phi_{00}$, where

$$\phi_{00} = G_1(1)G_1(2)G_2(3)\cdots G_n(2n)\alpha(1)\beta(2)\alpha(3)\cdots\beta(2n), \tag{1}$$

with an s-type spherical Gaussian of the form

$$G_i(j) = \left(\frac{2\alpha_i}{\pi}\right)^{3/4} \exp\left(-\alpha_i|\boldsymbol{r}_j - \boldsymbol{R}_i|^2\right), \tag{2}$$

with $\boldsymbol{R}_i$ the position of the centre of the ith Gaussian. The non-linear parameters $\{\alpha_i, \boldsymbol{R}_i\}$ are chosen to minimize the variational energy.

It turns out that when calculating the values of molecular properties, such as electric polarizability and magnetic susceptibility, good results may be obtained using perturbation theory [2] with ϕ_{00}, given in Eq. (1), rather than $\mathscr{A}\phi_{00}$. For the electric polarizability, results are generally good and those for pi-bonding systems can be improved by the use of p-type Gaussians rather than simulating them with s-type functions [3].

0040-5744/79/0051/0097/$02.00

The extension of this theory to the use of p-type Gaussians in the calculation of magnetic susceptibilities is more complex than might be expected due to degeneracy problems. It is the purpose of this paper to suggest various methods of dealing with these difficulties and to illustrate the methods by considering two pi-bonding systems, acetylene and ethylene.

2. Theory

When a magnetic field of magnitude $\mathscr{H}$ acts in the z-direction, there are two perturbations to the molecular Hamiltonian, given by

$$W^d = \tfrac{1}{8}\mathscr{H}^2 \sum_{i=1}^{2n} (x^2(i) + y^2(i)), \tag{3}$$

the diamagnetic part which is second order in the field, and

$$W^p = -\tfrac{1}{2}i\mathscr{H} \sum_{i=1}^{2n} \boldsymbol{k}\cdot\boldsymbol{r}(i) \wedge \nabla_i, \tag{4}$$

the paramagnetic part which is first order in the field. Each Gaussian, as given by Eq. (2), satisfies a one-electron eigenvalue equation

$$h_i G_i = \varepsilon_i G_i, \tag{5}$$

where $\varepsilon_i = 3\alpha_i$ and h_i is a 3-dimensional oscillator Hamiltonian

$$h_i = \tfrac{1}{2}\nabla^2 + 2(\alpha_i^2 |\boldsymbol{r} - \boldsymbol{R}_i|^2). \tag{6}$$

Consequently ϕ_{00} is an eigenfunction of the $2n$-electron Hamiltonian H_0, where

$$H_0 = \sum_{i=1}^{n} h_i(2i) + h_i(2i - 1). \tag{7}$$

From perturbation theory [2] the zz component of the magnetic susceptibility tensor of the molecule is

$$\chi_{zz} = -2\mathscr{H}^{-2}(E_{01}^d + E_{02}^p), \tag{8}$$

where

$$E_{01}^d = \langle \phi_{00} | W^d | \phi_{00} \rangle \tag{9}$$

and

$$E_{02}^p = \langle \phi_{00} | W^p | \phi_{01}^p \rangle, \tag{10}$$

with ϕ_{01}^p the first order change in the wavefunction due to the perturbation in Eq. (4), given by

$$(H_0 - E_0)\phi_{01}^p = (E_{01}^p - W^p)\phi_{00}, \tag{11}$$

where $E_{01}^p = \langle \phi_{00} | W^p | \phi_{00} \rangle$.

Now for s-type functions the paramagnetic term cancels out the origin-dependent part of the diamagnetic term, making the total result origin-independent. Then the formula for s-type spherical Gaussian Lewis sets is

$$\bar{\chi} = -\frac{1}{4}\sum_{i=1}^{n}\frac{1}{\alpha_i}. \tag{12}$$

We can consider the problem of Lewis basis sets which include p-type functions by an alternative method. Let the complete set of Gaussians that are eigenfunctions of Eq. (6) be $\{G^i_{mnp}\}$ where

$$G^i_{mnp} = N^i_{mnp}H_m(\sqrt{\alpha_i}x_i)H_n(\sqrt{\alpha_i}y_i)H_p(\sqrt{\alpha_i}z_i)\exp(-\alpha_i|\boldsymbol{r} - \boldsymbol{R}_i|^2), \tag{13}$$

with N^i_{mnp} the normalizing constant and $\{H_m\}$ are Hermite polynomials.

Instead of Eq. (6) we define

$$h_i = \varepsilon^i_{mnp}|G^i_{mnp}\rangle\langle G^i_{mnp}|, \tag{14}$$

with H_0 given by Eq. (7) as before but with the h_i in that expression for H_0 now given by Eq. (14).

The choice

$$\varepsilon^i_{mnp} = (2(m + n + p) + 3)\alpha_i, \tag{15}$$

in Eq. (14), exactly corresponds to taking the h_i of Eq. (6) but different choices of ε^i_{mnp} will lead to a different H_0 and consequently different results.

There are no problems in calculating the diamagnetic contribution to χ_{zz}, which is independent of the choice of H_0, but there are for E^p_{02} the paramagnetic part, which using Eq. (14) may be written

$$E^p_{02} = 2\sum_{i=1}^{n} e^{p''}_i, \tag{16}$$

with

$$e^{p''}_i = \mathscr{H}^2 \sum_{m,n,p}{}' \frac{\langle G^i|W^p|G^i_{mnp}\rangle\langle G^i_{mnp}|W^p|G^i\rangle}{\varepsilon^i - \varepsilon^i_{mnp}}, \tag{17}$$

where the sum excludes G^i, with $h_iG^i = \varepsilon^iG^i$. This is the usual "sum over states" formula, and if we take $G^i = G^i_{000}$ in conjunction with Eq. (15) we obtain the usual s-type Gaussian formula given in Eq. (12). Taking $G^i = G^i_{100}$, $G^i = G^i_{010}$ or $G^i = G^i_{001}$ corresponds to considering a p_x-, p_y- or p_z-type Gaussian respectively. We deal with two cases, double bonds and triple bonds, where a bond contains one or two p-type functions respectively. Of course, in both instances the bonds contain an additional s-type Gaussian, but this causes no problems and may be treated separately.

3. The Magnetic Susceptibility of Bonds Containing p-Type Gaussians

3.1. Double Bonds

A simple example of a molecule containing a double bond is ethylene, C_2H_4, which we take to be in the xz plane with the same geometry as before [3]. This means that the CC bond contains a p_y-type Gaussian, to represent the pi-bonding, which we now consider separately as the remaining contributions to $\bar{\chi}$ from the s-type Gaussians can be calculated using the original formula.

So we consider the case of a p_y-type Gaussian in a magnetic field. Whatever direction the field is in it is a simple matter to calculate the diamagnetic term which contains the same origin-dependent term as an s-type Gaussian. There is, however, an origin-dependent paramagnetic term for each direction which exactly cancels this, making the total contribution $\bar{\chi}_\pi$ to $\bar{\chi}$ from the p_y-type Gaussian origin-independent.

From Eqs. (14) and (17) the total contributions to $\bar{\chi}_\pi$ are

$$\chi_{\pi xx} = -\frac{1}{2\alpha} - (\varepsilon_{010} - \varepsilon_{001})^{-1}, \tag{18}$$

$$\chi_{\pi yy} = -\frac{1}{4\alpha}, \tag{19}$$

where α is the exponent and with $\chi_{\pi zz}$ the same as Eq. (18) with ε_{100} replacing ε_{001}. Then

$$\bar{\chi}_\pi = -\frac{5}{12\alpha} - \tfrac{1}{3}((\varepsilon_{010} - \varepsilon_{001})^{-1} + (\varepsilon_{010} - \varepsilon_{100})^{-1}). \tag{20}$$

If the ε_{mnp} in Eq. (20) are given by Eq. (15) then $\varepsilon_{100} = \varepsilon_{010} = \varepsilon_{001} = 5\alpha$ and there is obviously a singularity problem in Eq. (20) due to the occupied and unoccupied p-orbital energy levels being degenerate. Normally one would avoid this difficulty by using degenerate perturbation theory and take a linear combination of degenerate states. In the case of acetylene, to be considered shortly, it will be seen that to a certain extent ordinary degenerate perturbation theory can be used. For ethylene, however, ϕ_{00} is completely determined by the Frost model wavefunction which only contains a single p_y-type function. If the other p-type functions were present, then we could indeed take linear combinations. Since they are not, to avoid the degeneracy problem we redefine h_i, as given by Eq. (14), in such a way as to remove the degeneracy. This corresponds directly to choosing values for the differences $(\varepsilon_{010} - \varepsilon_{001})$ and $(\varepsilon_{010} - \varepsilon_{100})$, in Eq. (20), and by suitable choices of these differences we may obtain any result desired. Intuitively it is to be expected that ε_{010} should lie below ε_{100} and ε_{001} for C_2H_4 as it is the occupied level and so it can be seen that the paramagnetic contributions to $\bar{\chi}_\pi$ in Eq. (20), given in brackets, should be positive as usual. Obviously we wish to make reasoned choices, and so the problem really reduces to what sensible choices can be made for the energy levels of the p-orbitals. This will be discussed in Sect. 4.

3.2. Triple Bonds

A simple example is acetylene, C_2H_2, which we take to lie along the z-axis with the same geometry as before [3]. The CC bond contains a p_y- and a p_x-type Gaussian representing the pi-bonding, which we will again consider separately from the s-type Gaussians. Through symmetry considerations the occupied energy levels ε_{100} and

ε_{010} are the same for acetylene, posing problems if we use the same approach as for ethylene. Instead, following degenerate perturbation theory, we take linear combinations $p_x \pm ip_y$ to represent pi-functions and ϕ_{00} of Eq. (1) will be given by

$$\begin{aligned}\phi_{00} = {} & G_1\alpha G_1\beta \cdots (G_{p_x} + iG_{p_y})\alpha(G_{p_x} + iG_{p_y})\beta(G_{p_x} - iG_{p_y}) \\ & \times \alpha(G_{p_x} - iG_{p_y})\beta \cdots G_n\beta \end{aligned} \tag{21a}$$

in an obvious notation, rather than

$$\phi_{00} = G_1\alpha G_1\beta \cdots G_{p_x}\alpha G_{p_x}\beta G_{p_y}\alpha G_{p_y}\beta \cdots G_n\beta. \tag{21b}$$

The total contribution to $\bar{\chi}_\pi$ from Eqs. (14) and (17) using both $p_x + ip_y$ and $p_x - ip_y$ is

$$\bar{\chi}_\pi = -\frac{5}{6\alpha} - \tfrac{2}{3}(\varepsilon_{010} - \varepsilon_{001})^{-1} \tag{22}$$

and the problem again is where to choose the unoccupied energy level ε_{001} relative to the degenerate occupied level $\varepsilon_{010} = \varepsilon_{100}$.

4. Various Choices of h_i

4.1. Ethylene

As we have seen, the degeneracy problem can be avoided by choosing suitable and different values for ε_{100}, ε_{010}, ε_{001} (or their differences) and this is equivalent to choosing h_i of Eq. (14) suitably. We first consider three methods that require no extra computation, which we list before discussing. All are in conjunction with Eq. (20):

A $\varepsilon_{010} - \varepsilon_{001} = \varepsilon_{010} - \varepsilon_{100} = -4\alpha$
B $\varepsilon_{001} - \varepsilon_{100} = \infty$
C $\varepsilon_{010} - \varepsilon_{100} = -2n\alpha, \quad \varepsilon_{010} - \varepsilon_{001} = -2m\alpha; \quad n, m = 1, 2, \ldots$

Method A gives exactly the same contribution as for an s-type Gaussian and as Blustin [4] points out, since in the case of electric polarizabilities $\bar{\alpha}(p) = \bar{\alpha}(s)$, in an obvious notation, it would seem reasonable to assume that the same would apply in the magnetic case and $\bar{\chi}(p) = \bar{\chi}(s)$. Certainly there is a lot to be said for this argument on physical grounds, and this would mean that the formula of Eq. (12) would apply to basis sets including p-type Gaussians.

Method B involves removing the unoccupied levels to infinity, which reduces the contribution from the pi-system to the origin-independent diamagnetic contribution. Again, there are certain similarities with the s-type Gaussian case, as this is the only non-zero term in both instances, though with different factors multiplying α^{-1}.

The third method C corresponds to assigning values according to the eigenvalues of the harmonic oscillator Hamiltonian, as given by Eq. (6), which differ by multiples of 2α. Then, from Eq. (20), we write

$$\bar{\chi}_\pi^{n,m} = -\frac{5}{12\alpha} + \tfrac{1}{3}((2n\alpha)^{-1} + (2m\alpha)^{-1}) \tag{23}$$

we find $\bar{\chi}_\pi^{1,1} = -1/12\alpha$, $\bar{\chi}_\pi^{2,1} = \bar{\chi}_\pi^{1,2} = -1/6\alpha$ and $\bar{\chi}_\pi^{2,2} = -1/4\alpha$. These methods correspond to taking the values of ε_{100} and ε_{001} to be either one or two energy levels above ε_{010} with $\bar{\chi}_\pi^{2,2}$ yielding the same result as Method A.

Alternative methods of estimating the energy levels for the p-type Gaussians involve a recomputation of the wavefunction. Again we list the methods before discussing them. All are in conjunction with Eq. (20) once more:

D ε_{010} = highest occupied molecular orbital energy
$\varepsilon_{100}, \varepsilon_{001}$ = first and second virtual molecular orbital energies

(Virtual molecular orbital method (VMO))

E $\varepsilon_{010} - \varepsilon_{001} = (E_y - E_z)/2$; $\varepsilon_{010} - \varepsilon_{100} = (E_y - E_x)/2$

(Total energy method (TE))

F $\varepsilon_{100}, \varepsilon_{010}, \varepsilon_{001}$ = highest molecular orbital energy when there is a p_x-, p_y- or p_z-type Gaussian in ϕ_{00}

(Molecular orbital method (MO))

In ordinary molecular orbital perturbation theory, using for example uncoupled or coupled Hartree–Fock theory, the energy differences analogous to the ones given above in Eq. (20) are related to the differences between occupied and virtual molecular orbital energies. We cannot directly use this method with the Frost model since there are no virtual orbitals when a Lewis basis set is used. However, by adding p_x- and p_z-type Gaussians to the CC bond we create virtual orbitals. All parameters are held fixed at their optimum value with the exponents of the additional p-type functions the same as for the p_y-type Gaussian. It is now no longer a Lewis set calculation, and we may equate ε_{010} with the highest occupied molecular orbital energy and ε_{100}, ε_{001} with the virtual molecular orbital energies. This is Method D, denoted by VMO.

The other two methods retain a Lewis basis set. Initially the wavefunction $\mathscr{A}\phi_{00}^{y}$ for ethylene contains a p_y-type Gaussian

$$\phi_{00}^{y} = G_1\alpha G_1\beta \cdots G_{p_y}\alpha G_{p_y}\beta \cdots G_n\beta, \tag{24}$$

which gives a total energy E_y and the highest molecular orbital energy ε_y. Then, if instead of ϕ_{00}^{y} we use ϕ_{00}^{x} or ϕ_{00}^{z} with the same exponent as before, which involves substituting a p_x- or p_z-type Gaussian for the p_y-type Gaussian in Eq. (24), we obtain values for E_x, E_z, ε_x and ε_z. In these calculations all parameters are again held fixed at their optimum values given using the wavefunction containing the p_y-type Gaussian. For Method E we consider differences in the total energy (TE) and for Method F we allocate the energy levels according to the respective molecular orbital energy levels. For E the factor $\frac{1}{2}$ appears because of the double occupancy of each orbital.

4.2. *Acetylene*

The six methods in Sect. 4.1 can also be applied to C_2H_2, some directly and some with slight adaptations. This time the methods are in conjunction with Eq. (22):

A $\varepsilon_{010} - \varepsilon_{001} = -2\alpha \Leftrightarrow$ Using Eq. (12)

B $\varepsilon_{001} = \infty$

C $\varepsilon_{010} = \varepsilon_{001} = \varepsilon_{100} - \varepsilon_{001} = -2n\alpha$

Again we can write

$$\bar{\chi}_\pi^n = -\frac{5}{6\alpha} + \frac{1}{3n\alpha} \tag{25}$$

and $\bar{\chi}_\pi^1 = -1/2\alpha$ whilst $\bar{\chi}_\pi^2 = -2/3\alpha$. Since $\bar{\chi}_\pi$ refers to the contribution from two orbitals, $n = 1$ retrieves Eq. (12) whilst $n = 2$ gives a contribution of $-1/3\alpha$ per *p*-type Gaussian.

D $\varepsilon_{010} = \varepsilon_{100} =$ highest (degenerate) occupied molecular orbital energy
$\varepsilon_{001} =$ virtual molecular orbital energy (VMO)

E $\varepsilon_{010} - \varepsilon_{001} = (E_{xy} - E_{yz})/2$ (TE)
Substitute a p_z-type Gaussian for the p_x-type Gaussian

F $\varepsilon_{001} =$ highest occupied molecular orbital energy
$\varepsilon_{010} =$ second highest occupied molecular orbital energy (MO). Wavefunction as in E.

5. Results and Discussion

The calculations of the wavefunctions were performed using the OPIT program at Nottingham [5] with the fixed experimental geometries and orbital exponents as before [3]. The parameters required in Methods D, E, and F are given in Table 1, whilst Table 2 gives the results of applying the various methods and they are compared with experiment and other theoretical calculations given in the excellent review article by Ditchfield [6]. The last entry uses the wavefunction given by Frost and Rouse [7] in terms of just *s*-type functions using Eq. (12).

Method A, corresponding to using Eq. (12) for the mixed basis set, gives results very similar to those obtained using Frost's and Rouse's wavefunction and also the theoretical values of Pople. They are in reasonable agreement with experiment, underestimating for C_2H_2 and overestimating the magnitude for C_2H_4. It can be seen that there is not good agreement with experiment using Method B, corresponding to taking the origin-independent diamagnetic contribution, demonstrating that a positive origin-independent paramagnetic contribution is required. For Method C, the use of $\bar{\chi}_\pi^{2,1}$ for C_2H_4 and $\bar{\chi}_\pi^2$ for C_2H_2 give excellent results, whilst Methods D, E and F provide good results for one or other of the molecules but not both. In all instances results show a considerable improvement over SCF results and usually over CNDO and INDO.

Table 1. Parameters[a]

Method[b]	C_2H_4 Parameter	C_2H_4 Value	C_2H_2 Parameter	C_2H_2 Value
D (VMO)	ε_{100}	+0.6224	ε_{010}	−0.1869
	ε_{010}	−0.1567	ε_{001}	+0.6272
	ε_{001}	+0.7978		
E (TE)	E_x	−64.9572	E_{xy}	−64.7930
	E_y	−65.9567	E_{yz}	−63.9659
	E_z	−64.6559		
F (MO)	ε_{100}	+0.3284	ε_{010}	−0.1832
	ε_{010}	−0.1624	ε_{001}	+0.2748
	ε_{001}	+0.4656		

[a] All in atomic units. [b] See Section 4.

It is worth pointing out that it is not entirely clear as to the accuracy of the experimental results, as the theoretical results give $\bar{\chi}(C_2H_4) < \bar{\chi}(C_2H_2)$, taking the minus sign into consideration, which is the reverse of the experimental results. The use of formulae such as that of Kirkwood [8] which use $\bar{\alpha}$ to estimate $\bar{\chi}$ would certainly order it $\bar{\chi}(C_2H_4) < \bar{\chi}(C_2H_2)$. If we do accept the experimental results as being correct, which of the methods A–F is most suitable? Since the main attraction of the Frost model is its simplicity it is to be hoped that the formulae for properties would mirror this. For this reason we would recommend either Method A, using

Table 2. Average magnetic susceptibilities[a]

Method[b]	$\bar{\chi}$ C_2H_4	$\bar{\chi}$ C_2H_2
Experiment	−18.8 ± 0.8	−20.8 ± 0.8
Pople	−20.8	−17.8
CNDO	−17.7	−15.7
INDO	−15.7	−15.1
SCF	−40.4	−34.7
A (Eq. (12))	−21.2	−17.9
B (∞)	−25.1	−24.2
C ($\bar{\chi}_\pi^{1,1}$)	−17.2	−17.9 ($\bar{\chi}_\pi^1$)
C ($\bar{\chi}_\pi^{2,1}$)	−19.2	−21.0 ($\bar{\chi}_\pi^2$)
D (VMO)	−21.5	−20.3
E (TE)	−19.5	−16.5
F (MO)	−19.4	−17.2
Frost[c] (Eq. (12))	−20.7	−17.5

[a] 10^{-6} cgs units.

[b] First five results taken from Ref. [6]; see Section 4 for the other methods. (C_2H_4 in conjunction with Eq. (20), C_2H_2 with Eq. (22).)

[c] Wavefunction of Ref. [7].

the original formula, or Method C, for, as well, no additional computation is required. Furthermore, Methods D–F incorporate directly into the result the delocalized molecular orbitals, and it is to be hoped that changes in these will reflect similar changes in the localized orbitals. This is a drawback, as we are technically not using the correct orbitals for our theory, which requires localized ones.

Method A gives very reasonable results though Method C, using $\bar{\chi}_\pi^{2,1}$ and $\bar{\chi}_\pi^{2}$ for C_2H_4 and C_2H_2 respectively, does show an improvement. Moreover, in the latter case the formulae are still in terms of α^{-1}, the original orbital exponent, and we have simple expressions for $\bar{\chi}_\pi$. For aromatics, results seem to indicate that the original formula is adequate [9] due to the increased magnetic susceptibility of aromatics over aliphatics. From this, with $\bar{\chi}_\pi^{2,1}$ and $\bar{\chi}_\pi^{2}$, we find for hydrocarbons

$$\bar{\chi} = -\frac{1}{4}\sum_{s,p_A=i}\frac{1}{\alpha_i} - \frac{1}{6}\sum_{p_D=i}\frac{1}{\alpha_i} - \frac{1}{3}\sum_{p_T=i}\frac{1}{\alpha_i}, \tag{26}$$

where the first sum is over all s- and aromatic p-type functions, the second over p-type functions in double bonds and the third over p-type Gaussians in triple bonds. All orbitals are assumed to be doubly occupied.

Wavefunctions using elliptical Gaussians rather than spherical ones, as given by Eq. (2), are considerably rarer. Expressions for $\bar{\chi}_\pi$ for both C_2H_4 and C_2H_2 using elliptical Gaussians are given in the appendix, but results using the wavefunctions of van Duijnen and Cook [10] are poor, where once more it is the paramagnetic part that causes problems.

6. Anisotropies

Since the contributions for the three axes are no longer identical we may also calculate the anisotropy of χ_π, which is defined as $\Delta\chi_\pi = \chi_{\pi\parallel} - \chi_{\pi\perp}$ and following Ditchfield [6] for C_2H_4 we take

$$\Delta\chi_\pi = \chi_{\pi_{xx}} - \tfrac{1}{2}(\chi_{\pi_{yy}} + \chi_{\pi_{zz}}). \tag{27}$$

Using $\bar{\chi}_\pi^{2,1}$ from Eq. (23), or $\bar{\chi}_\pi^{1,2}$ which will give the same result for $\bar{\chi}_\pi$, we find $\Delta\chi_\pi = +1/4\alpha$ or $-1/8\alpha$, which is $+6.0$ or -3.0 in 10^{-6} cgs units respectively. The estimates for $\Delta\chi$, that is for the whole molecule, defined by $\Delta\chi = \chi_\parallel - \chi_\perp$ and in this case the formula of Eq. (28) omitting the subscript π, vary between $+8.7$ and $+11.8$ [8] and so it would seem that $\bar{\chi}_\pi^{2,1}$ is the one to use. Of course, there may well be additional anisotropic contributions from other parts of the molecule, but all other terms for s-type spherical Gaussians are isotropic and so only the anisotropy of the pi-contribution can be given.

For C_2H_2 we define $\Delta\chi_\pi$ by [6]

$$\Delta\chi_\pi = \chi_{\pi_{zz}} - \tfrac{1}{2}(\chi_{\pi_{yy}} + \chi_{\pi_{xx}}) \tag{28}$$

and for $\bar{\chi}_\pi^{2}$ of Eq. (25) we find $\Delta\chi_\pi = -5/12\alpha$, which is -7.8 in 10^{-6} cgs units, in excellent agreement with the experimental value of -7.7 [11], but other theoretical estimates put the value between -10.1 and -19.4 [6].

For both C_2H_4 and C_2H_2, using the estimates of $\Delta\chi_\pi$ above, assuming that $\Delta\chi = \Delta\chi_\pi + \Delta\chi_\sigma$, then in view of results above $\Delta\chi_\sigma$ will be small. Of course in our case $\Delta\chi_\sigma = 0$, but it appears that $\Delta\chi_\pi$ provides a reasonable estimate of $\Delta\chi$ when compared with the experimental value for C_2H_2 and theoretical values for C_2H_4. This is rather a simplistic view on a subject on which there has been much debate, see for instance Ditchfield [6] or Davies [12], for which different formulae for $\Delta\chi$ have been suggested, including χ_π and $\Delta\chi_\sigma + \Delta\chi_\pi + \chi_\pi$, though these tend to be used rather more for ring systems. We feel, however, that the results for the anisotropies using Method C provide further evidence to support their use and that Eq. (26) should provide better estimates than the original formula.

Acknowledgements. I would like to thank the SRC for the award of a postdoctoral fellowship and Dr. Terry Amos for discussions and a critical reading of this paper.

Appendix. Formulae Using Elliptical Gaussians

C_2H_4:

$$\chi_{\pi_{xx}} = -\frac{3}{8\beta} - \frac{1}{8\gamma} + \left\{\frac{1}{4}\frac{(\gamma-\beta)^2}{\beta\gamma(\beta+\gamma)} + \frac{(\gamma+\beta)^2}{8\gamma\beta(\gamma-\beta)}\right\}$$

$$\chi_{\pi_{yy}} = -\frac{1}{8\alpha} - \frac{1}{8\gamma} + \left\{\frac{(\gamma-\alpha)^2}{8\alpha\gamma(\alpha+\gamma)}\right\}$$

with $\chi_{\pi_{zz}}$ the same as $\chi_{\pi_{xx}}$ with α replacing γ, where α, β and γ are the exponents of the p_y-type Gaussian in the x-, y- and z-directions. The paramagnetic origin-independent contribution is given in brackets.

C_2H_2:

$$\chi_{\pi_{xx}} = -\frac{1}{2\alpha} - \frac{1}{4\gamma} + \left\{\frac{3(\alpha-\gamma)^2}{8\alpha\gamma(\alpha+\gamma)} + \frac{1}{8\alpha\gamma}\frac{(\alpha+\gamma)^2}{(\gamma-\alpha)}\right\}$$

$$\chi_{\pi_{zz}} = -\frac{1}{\alpha}$$

with $\chi_{\pi_{yy}} = \chi_{\pi_{xx}}$ as $\beta = \alpha$.

References

1. Frost, A. A.: J. Chem. Phys. **47**, 3707 (1967)
2. Amos, A. T., Yoffe, J. A.: J. Chem. Phys. **63**, 4723 (1975)
3. Yoffe, J. A.: Chem. Phys. Lett. **54**, 562 (1978)
4. Blustin, P. H.: private communication
5. Ford, B., Hall, G. G., Packer, J. C.: Intern. J. Quantum Chem. **4**, 533 (1970)
6. Ditchfield, R.: MTP Intern. Rev. Sci. Phys. Chem. Series 1, **2**, 91 (1972) (ed. G. Allen)
7. Frost, A. A., Rouse, R. A.: J. Am. Chem. Soc. **90**, 1965 (1968)
8. Kirkwood, J. G.: Physik. Z. **33**, 57 (1932)
9. Blustin, P. H.: Mol. Phys. *36*, 279 (1978)
10. van Duijnen, P., Cook, D. B.: Mol. Phys. **21**, 475 (1971)
11. Cederberg, J. W., Anderson, C. H., Ramsey, N. F.: Phys. Rev. **A136**, 960 (1964)
12. Davies, D. W.: The theory of the electric and magnetic properties of molecules. New York: Wiley 1967

Received October 2, 1978