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The Effect of the Charge Density on the Dipole Moment of Diatomic Molecules

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Abstract The aim of the present work is to improve the results of the calculation, using the Variational Cellular Method (VCM), of the electric dipole moment of several diatomic molecules. In previous calculations, the electronic charge density was treated like a spherically symmetric function in the inscribed sphere within each cell and as being the same constant value For all intercellular regions. Since the results obtained with such an approximation have not been satisfactory, an improved approximation for the charge density in the intercellular regions is needed. This work consists of considering the charge density still constant outside the inscribed sphere but with different values in each intercellular region. A new expression for the dipole momentisobtained, and applied to the diatomic molecules HF, CO, BF and CS. In addition, the corresponding dipole moment curves, potential energy curves and spectroscopic constants are calculated taking into consideration our approximation and the traditional approximation for the charge density, The results of the two models are compared with each other and with experimental results for all the molecules considered.

1. INTRODUCTION

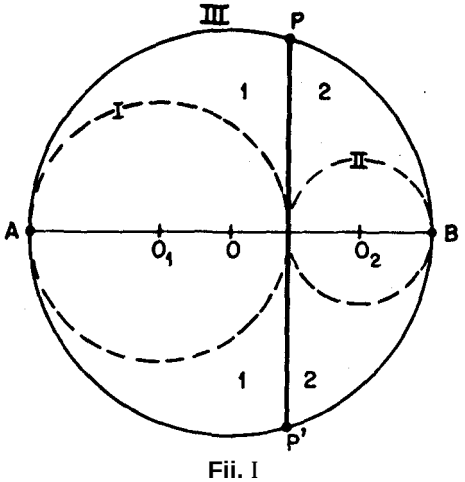
In a previous paper[1] we calculated the electric dipole moment of some diatomic molecules using the Variational Cellular Method (VCM). In that calculation the molecular space was divided into cells, one cell for each atom of the molecule, and third cell, the external one, encircling the two atomic cells. The nuclear charge was considered as a positive point charge, located at the center of the inscribed sphere in each atomic cell. The electronic charge was taken to be spherically symnetric inside this sphere and constant in the whole region between the inscribed sphere ans corresponding atomic cell. This kind ofapproximation for the electronic charge, commonly called the muffin-tin approximation, has already been used before[2] in a multiple scattering Xa (MS-Xα) calculation of the electric dipole moment of diatomic molecules. The muffin-tin approximation, either in the context of the VCM as was donein reference 1 or with the MS-Xα as in reference 2, did not present good re-

sults for the electric dipole moment, For some molecules the error was of the order of the moment itself, thus being unacceptably large[1,2].

However, one possible reason for the inadequacy of the results obtained in reference 1 could be the way in which the muff'in-tin charge approximation was used. There, the negative charge inside each inscribed sphere and the charge in the external charge werr calculated and added up. The result was subtracted from the positive (nuclear) charge of the molecule. The resulting net charge was distributed uniformly in the intercellular regions 1 and 2 of fig.1, giving a constant and equal value for the charge density in the whole intercellular region.

It seems more reasonable to proceed differently, specially in the case of heteronuclear diatomic molecules, by allowing the constant value of the charge density in the intercellular region 1 to be different from the constant value of this quantity in region 2.

To accomplish this, the net charge mentioned above is calculated for each atomic cell and, instead of adding them up as bsfore, each remaining charge is distributed uniformly over its correspondly intercellular region. The intercellular regions have constant densities but these constant values are not equal as before.



Fii. I

Fig.1 - Regions ofthemolecular space separated by the plane PP'. I and II are atomic cells, III is the external cell, 1 and 2 are the intercellular regions, and O_1 and O_2 are the center of the inscribed spheres in each atomic cell.

It is expected that with this new way of applying the muffin--tin charge density approximation the more unlike the atoms of the diatomic molecule are the more relevant to the calculation they are in order to check these ideas and see their effects on the behaviour of the charge densities, potential curves, total charges, dipole moments etc. we have performed the calculations described in the following.

2. ELECTRIC DIPOLE MOMENT CALCULATION

The electric dipole moment $\vec{\mu}$ of a molecule is the sum of the electronic contribution to the electric dipole moment, $\vec{\mu}_e$, plus the contribution from the positive or nuclear charges, $\vec{\mu}_N$, that is,

$$\vec{\mu} = \vec{\mu}_e + \vec{\mu}_N \quad . \tag{1}$$

The electronic and nuclear part of the dipole moment are given by

$$\vec{\mu}_e = - \int_V \rho_e(\vec{r})\vec{r}d^3r \tag{2}$$

and

$$\vec{\mu}_N = \int_V \rho_N(\vec{r})\vec{r}d^3r \quad , \tag{3}$$

where $\rho_e(\vec{r})$ and $\rho_N(\vec{r})$ are the electronic charge density and the positive charge density at position $\vec{r}$ respectivelly, and V is the volume of the molecule, or the molecular space.

The molecular space V is divided into atomic cells according to fig. 1. The atomic cell I is the spherical callote PAP' located at the left of the separating plane PP' and it encircles the first atom of the molecule situated at O,. The dotted sphere inside cell I whose center is O, is called the inscribed sphereof the cell I. On the other side of the plane PP' we have the atomic cell II which surrounds the second atom of the rnolecule located at O_2 and we have also theinscribed sphere centered at O_2. Surrounding cell I and cell II is the atomic cell III which is the external region of the sphere whose center is O and whose radius is OA. The intercellular region 1 is the region located at the left of the plane PP' between the atomic cell I and its corre-

sponding inscribed sphere. The analogous region on the other side of the plane PP' is the intercellular region 2.

In these various regions of the space we assume the following dependence for the electronic charge density. It is spherically symmetric inside each inscribed sphere with respect to the center O_1 or O_2 of the corresponding sphere, it is constant in the intercellular regions 1 or 2 of fig. 1, and finally, it is spherically symmetric in the external region III of that figure with respect to the center O of the external sphere. Even though the origin of the vector $\vec{r}$ in fig. 2 is arbitrary because the total charge of the molecule is zero, it is taken to be the point O of figure 1. Expressions (2) and (3) are written in units of the electron charge e. The positive charges of the molecule are located at the nuclear poisitions which are the centers O_1 and O_2 of fig. 1, and the density $\rho_N(\vec{r})$ can be written as

$$\rho_N(\vec{r}) = Z_1\delta(\vec{r} - \vec{d}_1) + Z_2\delta(\vec{r} - \vec{d}_2) \ , \qquad (4)$$

where Z_1 and Z_2 are the number of protons of atom 1 and 2 of the diatomic molecule, and $\vec{d}_1$ and $\vec{d}_2$ are the vectors from the origin O to the centers O_1 and O_2, respectivelly, according to fig. 2.

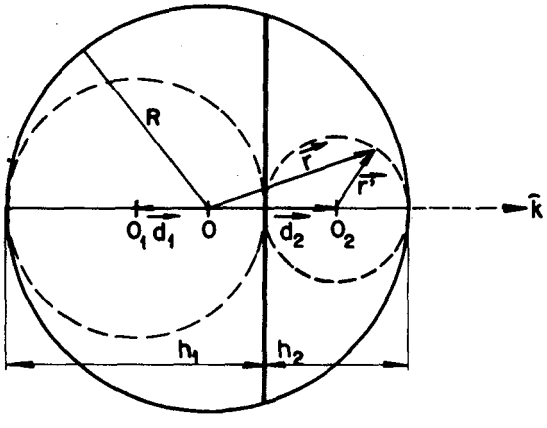


Fig 2

Fig.2 - The vector position $\vec{r}$ with respect to the center of cell III. With respect to O_2, the same point has $\vec{r}' = \vec{r} - \vec{d}_2$.

To compute $\vec{\mu}_e$, eq. (2), taking into considerations the model assumed For the electronic charge density $\rho_e(\vec{r})$, we have to compute the integral of eq. (2) in each one of the distinct regions of the molecular space, and then add the integrals from the separates regions. Insidethe inscribed spheres of centers O_1, O_2 and 0, the value of the integral (2) is respectivelly, $Q_1\vec{d}_1$, $Q_2\vec{d}_2$ and zero, where the vectors $\vec{d}_1$ and $\vec{d}_2$ are shown in fig. 2, and Q_1 and Q_2 are the total electronic charges inside the spheres of center O and O_2 [3]. To perform integral (2) in the intercellular regions 1 and 2, let us do it for region 2 only, since the procedure can be repeated easily later on for region 1. The volume of the intercellular region 2 can be considered as the difference between the volume of the whole cell II, which is V_{II} minus the volume of the inscribed sphere which we call Ω_2. If $\bar{\rho}_2$ is the constant value of the charge density in the region Ω_2, then we can write that

$$\int_2 \bar{\rho}_2 \vec{r} d^3r = \int_{V_{II}} \bar{\rho}_2 \vec{r} d^3r - \int_{\Omega_2} \bar{\rho}_2 \vec{r} d^3r \quad . \tag{5}$$

According to fig. 2 the vector position r can be written as $r = r' + d$, and substituting this value in the last integral of equation (5), that integral turns out to be

$$\int_{\Omega_2} \bar{\rho}_2 \vec{r} d^3r = \bar{\rho}_e \Omega_2 \vec{d} \quad , \tag{6}$$

where the volume Ω_2 is equal to $4\pi/3\ (h_2/2)^3$ where h_2 is the diameter of the inscribed sphere two, shown in fig. 2. The first integral of the right hand side of eq. (5) can be written as

$$\int_{V_{II}} \bar{\rho}_e \vec{r} d^3r = \bar{\rho}_e\ V_{II} \vec{R}_2 \quad , \tag{7}$$

where V_{II} is the volume of the atomic cell II. This atomic cell is a callote of a sphere of radius R, where $2R = h_1 + h_2$, and its volume is given by

$$V_{II} = \frac{\pi}{3} h_2^2 (3R - h_2) \quad . \tag{8}$$

The vector $\vec{R}_2$ is the vector which defines the position of the center of mass of the cell II, and it can be shown that its value is

$$\vec{R}_2 = \frac{3}{4}\,\frac{(2R - h_2)^2}{(3R - h_2)}\,\hat{k} \quad . \tag{9}$$

The unit vector $\hat{k}$ is along the symmetry axis of the molecule. The radii a_1 and a_2 of the spheres of centers O_1 and O_2 are $a_1 = h_1/2$ and $a_2 = h/2$, and they can be written as $\vec{d}_1 = -a_2\hat{k}$ and $\vec{d}_2 = a_1\hat{k}$. Taking into account these observations and substituting eqs. (9) and (8) into (7) we obtain, after some algebraic manipulations, that

$$\int_{V_{II}} \bar{\rho}_e \vec{r}\, d^3r = a_1 \vec{Q}_2 \hat{k} \quad , \tag{10}$$

where the total negative charge $\bar{Q}_2$ inside region 2 can be written as $\bar{Q}_2 = \rho_2(V_{II} - \Omega_2)$. Taking the results of eqs. (10) and (6) into eq. (5) we obtain

$$\int_2 \bar{\rho}_2 \vec{r}\, d^3r = -\bar{Q}_2\left(\frac{a_2}{3} - a_1\right)\hat{k} \quad . \tag{11}$$

Proceeding exactly in the same way for intercellular region I, we obtain the result

$$\int_1 \bar{\rho}_1 \vec{r}\, d^3r = -\bar{Q}_1\left(a_2 - \frac{a_1}{3}\right) E \quad , \tag{12}$$

where $\bar{Q}_1$ is the total electronic charge located in the intercellular region 1 of fig. 1. Adding the results expressed by equations (12) and (11) with the contributions coming from the three inscribed spheres which, as we mentioned before, are $Q_1\vec{d}_1$, $Q_2\vec{d}_2$ and zero, we obtain the electronic contribution to the electric dipole moment of the molecule, which is

$$\vec{\mu}_e = \left[\bar{Q}_2\left(\frac{a_2}{3} - a_1\right) + \bar{Q}_1\left(a_2 - \frac{a_1}{3}\right) + Q_1 a_2 - Q_2 a_1\right]\hat{k} \quad . \tag{13}$$

The nuclear contribution to the electric dipole moment of the molecule can be calculated very easily by substituting eq. (4) into eq. (3). Proceeding in this way, the nuclear contribution to the dipolei mo-

ment turns out to be

$$\vec{\mu}_N = (-Z_1 a_2 + Z_2 a_1)\hat{k} \ . \qquad (14)$$

The total dipole moment of the molecule is the sum of the expressions (13) and (14), which, after arranging the terms, becomes

$$\vec{\mu} = \left[(Z_2 - Q_2 - \bar{Q}_2 - \frac{\bar{Q}_1}{3})a_1 - (Z_1 - Q_1 - \bar{Q}_1 - \frac{\bar{Q}_2}{3})a_2\right]\hat{k} \ . \qquad (15)$$

In the above expressions we have the electric dipole moment of a diatomic molecule for a geometry like than of fig. 1, Z_i are the positive point charges located at the centers O_1 and O_2 of the inscribed spheres of fig. 1, Q_i are the total electronic charges inside the inscribed spheres, and $\bar{Q}_i$ are the electronic charges in the intercellular regions 1 and 2 of fig. 1 when the charge density in these regions are constant but different from one region to another. If the chargedensity takes the same value $\bar{Q}$ in both regions 1 and 2, then expression (15) turns out to be

$$\vec{\mu} = \left[(Z_2 - Q_2 - \bar{Q}/3)a_1 - (Z_1 - Q_1 - \bar{Q}/3)a_2\right]\hat{k} \ . \qquad (16)$$

Appropriately enough, expression (15) immediately reduces to the expression used in reference (1) when the charge densities in the intercellular regions 1 and 2 of fig. 1 are constrained to be equal. This latter expression (16) is the expression used in reference (1). It is also convenient to note that equations (15) and (16) can be used to obtain the dependence of the electric dipole moment with respect to the internuclear distance R within the respective conditions on the density since every quantity in those equations, except for Z_i, varies with R. It should be noted that the vector $\vec{\mu}$ is a vector parallel to the symmetry axis of the molecule and it can be directed from atom 1 to atom 2, that is, from left to the right, when the coefficient of the vector $\hat{k}$ in eq. (15) or (16) is a positive quantity, or in the reverse sense, when this quantity is negative.

From the results of our calculations it was possible to establish, for all molecules considered, that whenever the net charge on the

left side of the separation plane PP' of fig. 1 was negative, and consequently the right side was positive, the resulting quantity was positive. This allows us to say that a positive dipole moment implies $A^- B^+$ when atom A is placed in the cell I and B in cell II.

3. APPLICATIONS

A. HF Molecule

The input data necessary to perform a VCM calculation for the HF molecule are the same as the ones used in reference (1), which are: the ground state is $X^1\Sigma^+$ which corresponds to the closed shell electronic configuration $1\sigma^2 2\sigma^2 3\sigma^3 1\pi^4$; the experimental internuclear separation in the ground state is R_e = 1.733 a_0 (a_0 is the Bohr radius and it is equal to 0.529 10 cm); the radii a_1 and a_2 of the inscribed spheres are proportional to the covalent radii of the correspondent atoms which are a_1 = 1.1789 a_0 for Fluorine and a_2 = 0.5541 a_0 for Hydrogen; the exchange-correlation parameters a are the ones obtained by Schwarz[5], except for the Hydrogen whose value is taken as α_2 = 0.7723. For Fluorine α_1 = 0.7373.

In table 1 we present the numerical values of the total energy of the HF molecule as a function of the internuclear distance R, using the two approximations for the charge density mentioned before. The calculated equilibrium internuclear distance % is approximately the same for the two models, both values being above the experimental result, 21% when the charge density is the same in regions 1 and 2 of fig. 1, and 19% when the charge density in these regions is different.

In table 2 we present the numerical values of the electric dipole moment from eqs, (15) and (16) for several values of the internuclear distance, using the two models for the charge density,

The curves corresponding to table 2 are shown in fig. 3.

From table 2 we can obtain the value of the dipole moment at the calculated equilibrium separation for each model of the charge density. For the case (a) of that table, the equilibrium separation is R_C = = 1.21, R_e = 2.0969 a_0 and the value obtained for μ is $\mu(R_e)$ = 0.743D, while for case (b), R_e = 1 19, R_e = 2.0623 a_0 and μ is given by $\mu(R_e)$ = = 1.403 D. The experimental result forp is μ = 1.797D [6] and it is a

Table 1 - Numerical values of the total energy if the HF molecule in the ground state as a function of the interatomic distance αR_e (R_e=1.733 a_0), using both models for the charge density. Energies are in Ridberg and distances are in atomic units.

α	MCV(a)	MCV(b)	α	MCV(a)	MCV(b)
0.70	-199.5739	-199.6781	1.17	-200.4253	-200.3420
0.80	-199.9629	-200.0020	1.18	-	-200.3424
0.85	-200.0913	-200.1000	1.19	-200.4270	-200.3431
0.92	-200.2445	-200.2333	1.20	-200.4271	-200.3426
0.95	-200.2892	-200.2440	1.21	-200.4272	-200.3424
1.00	-200.3323	-200.2794	1.22	-200.4270	-
1.02	-200.3500	-200.9216	1.23	-200.4262	-200.3411
1.04	-200.3651	-200.3020	1.25	-200.4243	-200.3391
1.06	-200.3779	-200.3104	1.27	-200.4214	-200.3364
1.08	-200.3888	-200.3177	1.29	-200.4176	-200.3329
1.10	-200.4008	-200.3261	1.31	-200.4132	-200.3291
1.13	-200.4181	-200.3383	1.33	-200.4083	-200.3250
1.15	-200.4228	-200.3410	1.35	-200.4015	-200.3199

a) The charge density is the same in regions 1 and 2 of fig. 1. b) The charge density is not the same in regions 1 and 2 of fig. 1.

Table 2 - Numerical values of the dipole moment of the HF molecule in the ground state, as a function of the interatomic distance αR_e, where R_e = 1.773 a_0, using both approximations for the charge density. Dipole moments are given in Debye and the distances in atomic units.

α	MCV(a)	MCV(b)	α	MCV(a)	MCV(b)
0.70	-2.730	-2.273	1.17	0.427	1.252
0.80	-2.233	-1.629	1.18	-	1.327
0.85	-1.936	-1.282	1.19	0.584	1.403
0.92	-1.460	-0.798	1.20	0.663	1.484
1.00	-0.889	-0.113	1.21	0.743	1.563
1.02	-0.734	0.045	1.22	0.823	-
1.04	-0.584	0.210	1.23	0.896	1.722
1.06	-0.429	0.370	1.25	1.054	1.871
1.08	-0.275	0.530	1.27	1.211	2.026
1.10	-0.120	0.690	1.29	1.365	2.181
1.13	0.114	0.937	1.31	1.521	2.330
1.15	0.272	1.096	1.33	1.676	2.477
			1.35	1.829	2.630

a) The charge density is the same in the regions 1 and 2 of fig.1. b) The charge density is not the same in the regions 1 and 2 of fig. 1.

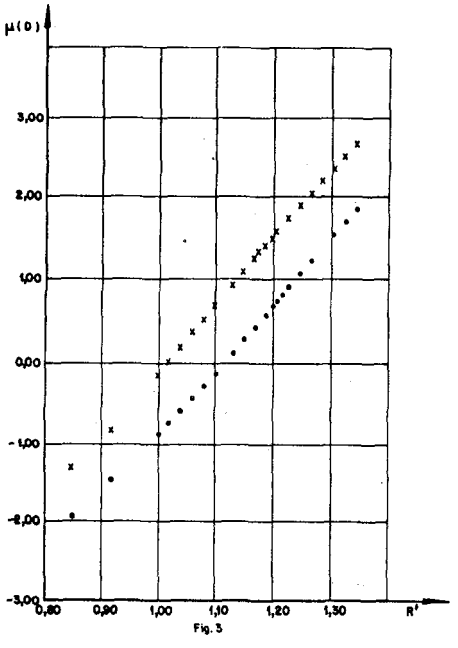


Fig.3-Dipole moment curveof HF.The dotted curve corresponds to eq. (16) and crossed curve to eq. (15) of the text, R' means $R \times 1.733$ wherê R is the internuclear distance.

vector that goes from the F^- atom to the H^+ atom.

Performing a least-square fitting of the dipole moment curves shown in fig. 3 toaquadratic equation, weobtain the following expressions for μ when the approximations a and b of table 2 are used,

$$\mu_a = 0.74 + 4.83\ \rho + 0.95\ \rho^2 ,$$

$$\mu_b = 1.42 + 4.48\ \rho - 0.096\ \rho^2 .$$

Here, ρ is given by $\rho = R - R_e$, R_e is the calculated equilibrium distance in units of a, and μ is expressed in Debye. In reference 7 the experimental expression for the quadratic equation obeyed by μ is

$$\mu = 1.797 + 0.805\ \rho + 0.038\ \rho^2$$

while the Hartree-Fock results, mentioned there, are

$$\mu = 1.911 + 1.012\ \rho + 0.065\ \rho^2 \ .$$

In case b the value of the dipole moment and its second derivative with respect to the internuclear distance are in a much better agreement with the experimental results than in case a. However, the first derivative of μ is poorly calculated in both cases.

To observe the dependence of the spectroscopical constant of the HF molecule with respect to the model assumed for the charge density, we can obtain some of these constants from the potential curve whose numerical values are given in table 1. The results are shown in table 3, where C_e is the equilibrium distance, D_e the dissociation energy, ω_e the vibrational frequency and E the total energy at R_e.

Table 3 - Spectroscopical constants of the HF molecule .in the ground etate.

	MCV(a)	MCV(b)	MCV(c)
$C_e(a_0)$	2.0969	2.0623	1.7330
D_e(eV)	8.28	7.13	6.40
$\omega_e(cm^{-1})$	4342	4287	4138
E(Ry)	-200.4272	-200.3431	-201.0540

a) The charge density is the same in region 1 and 2 of fig. 1. b) The charge density is not the same in region 1 and 2 od fig. 1. c) Ref. 8.

B. Other Molecules

The same kind of calculations as presented for HF areperformed for other diatomic molecules: CO, BF and CS. These molecules have been chosen because when we go from CO to CS, passing by BF, we may roughly say that we are going from a "less" heteronuclear to a "more" heteronuclear molecule. We should expect that the model of dlstinct values for the charge density as presented herein should increase its relevance when studying these molecules in this order.

In table 4 we present the input data necessary to perf'orm a Variational Cellular Method calculation of the molecules BF, CO and CS.

Table 4 - Input parameters necessary to perform a VCM calculations. The meaning of the parameters are the same as those used for HF. Distances are in atomic units.

	BF	CO	CS
GS	$KK1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2$	$KK1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2$	$KKL1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2$
R_e (a)	2.3847	2.1320	2.8995
	1.3806	1.1491	1.2341
α_2	1.0041	0.9829	1.6654
α_1 (b)	0.7653	0.7593	0.7593
α_2	0.7373	0.7115	0.7248

a) Reference 9. b) Reference 5.

Having arrived at the potential curves for these molecules within this model, the calculated equilibrium distances are obtained. The electric dipole moment is calculated as a function of the interatomic distance for several values of R, as well as at R_e (experimental equilibrium distance). In tables 5, 6 and 7 we present the values of μ for these molecules calculated only at the two points R_e and R_c.

The dipole moment curves of BF, CO and CS are shown in fig. 4 for both conditions on the charge density. When the charge density assumes the same constant value in regions 1 and 2 of fig. 1, the dotted curves in fig. 4 are obtained. The curves with crosses in these figures correspond to different values of the charge density in regions 1 and 2 of fig. 1. The curves are almost linear and if we perform a fitting to a quadratic equation, we obtain the following best fits for the dipole moments, corresponding to the crossed curves of fig. 4.

$$\mu_{CO} = -0.84 - 13.28\ \rho + 4.56\ \rho^2\ , \qquad (17a)$$

$$\mu_{BF} = 0.71 - 16.95\ \rho + 15.04\ \rho^2, \qquad (17b)$$

Table 5 - Values of the electric dipole moment of CO attheexperimental and calculated equilibrium internuclear distance, in Debye units.

	$\mu(D)^{(a)}$	$\mu(D)^{(b)}$	$\mu(D)^{(f)}$
R_e (c)	-2.124	-1.534	0.11
0.95 $R_e^{(d)}$	-	-0.842	-
1.05 $R_e^{(e)}$	2.239	-	-

a) When using eq, (16). b) When using eq. (15). c) R_e is the experimental value of the internuclear equilibrium distance and is equal to 2.132 a_0. d) Calculated equilibrium distance when the electric charge density is not the same in the intercellular region. e) Calculated equilibrium distance when the electric charge density is the same in the intercellular region. f) Experimental value, see ref. 9.

Table 6 - Value of the dipole moment of BF at the experimental and calculated equilibrium internuclear distance in Debye units.

R	$\mu(D)^{(a)}$	$\mu(D)^{(b)}$	$\mu(D)^{(f)}$
$R_e^{(c)}$	3.252	-2.124	0.5
0.83 $R_e^{(d)}$	-	0.709	-
1.13 $R_e^{(e)}$	1.591	-	-

a) Value of $\vec{\mu}$ when using eq. (16). b) Value of $\vec{\mu}$ when using eq. (15). c) R_e = 2.3847 a_0. d) Calculated value of R_e when the charge density is not the same in the intercellular region. e) Calculated value of R_e when the charge density is the same in the intercellular region. f) Experimental value.

$$\mu_{CS} = 1.96 - 22.00\ \rho - 33.30\ \rho^2 \ . \qquad (17c)$$

The best fits to the dotted curves of fig. 4 give the following expressions for the dipole moments

$$\mu_{CO} = 1.62 - 8.69\ \rho - 2.20\ \rho^2 \ , \qquad (18a)$$

$$\mu_{BF} = 1.72 - 10.53\ \rho + 20.88\ \rho^2 , \qquad (18b)$$

$$\mu_{CS} = 0.92 - 13.86\ \rho + 18.15\ \rho^2 . \qquad (18c)$$

The quantity ρ in the expressions above is not the same as before. Here ρ is given by $\rho = (R-R_C)/R_C$, where R_C is the calculated equilibrium interatomic distance.

The set of eqs. (17) presents the R dependence of up to second order in ρ for the CO, BF and CS molecules when the model assumed for the charge density is the one which gave rise to eq. (15), while the set of eqs. (18), is the ρ dependence of eq. (16). A SCF calculation performed by W.M. Huo[10] for CO and BF generated the following curves:

$$\mu_{CO} = 0.158 + 5.4\ \rho + 1.7\ \rho^2 \ ,$$

$$\mu_{BF} = -\ 1.05 + 6.9\ \rho + 4.3\ \rho^2 \ ,$$

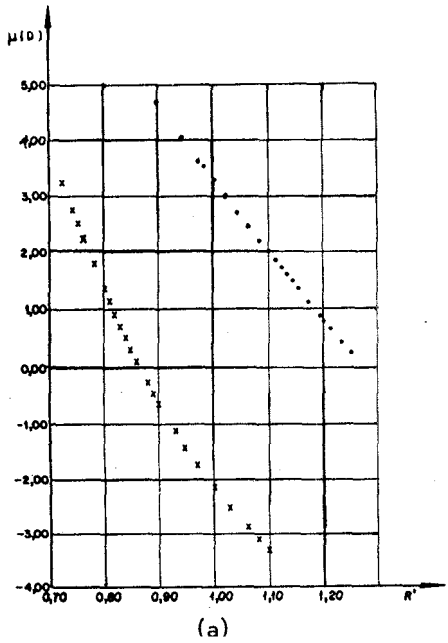
while the curve representing the experimental results for CO is given by[11]

$$\mu_{CO} = \mp\ 0.112 + 3.35\ \rho + 9.40\ \rho^2 .$$

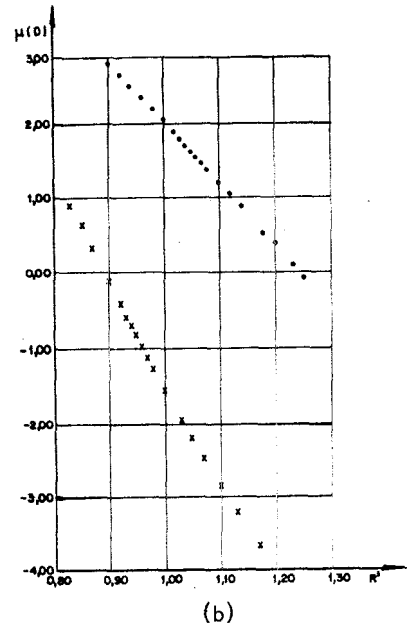
We could not find in the literature experimental results for BF and CS for comparison.

4. DISCUSSIONS

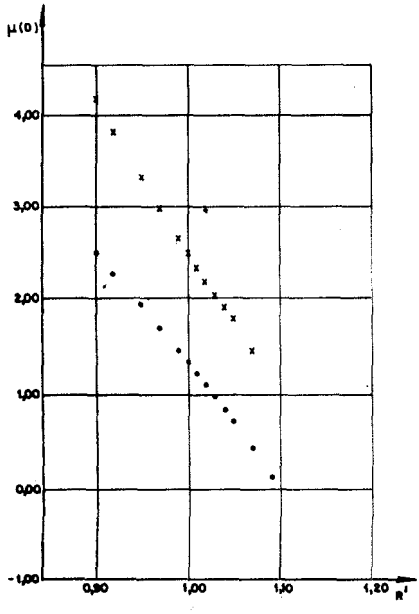
It is a fact that the dipole moment is a very sensitive quantity and it appears that its dependence with R is poorlycalculated for almost all molecules by SCF methods[12]. As far as we know, this is the



(a)



(b)



(c)

Fig.4 - Dipole moment curves for: (a) CO; (b) BF; (c) CS. The dotted and crossed curves correspond to eq. (16) and eq. (15) of the text. R' means: (a) $2.3847 \times R$; (b) $2.132 \times R$; (c) $2.898 \times R$; R being the internuclear distance.

first time that a cellular method is used to compute μ or its dependence upon R. The results as the majority of the other methods, are not satisfactory concerning the first and the second derivatives of μ with respect to the internuclear distance. At the equilibrium distance, theresultsare reasonable and agree well-with the experimental data available. We conclude that the method considered herein enables one to calculate with relative precision and simplicity the electric dipole moment of a diatomic molecule at the equilibrium position.

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Resumo

O objetivo do presente trabalho é melhorar o resultado dos cálculos, usando o Método Celular Variacional (MCV), do momento do dipólo elétrico de algumas moléculas diatômicas. Em trabalhos anteriores a densidade de carga eletrônica foi tratada como uma função esféricamente simétrica no interior da esfera inscrita de cada célula e como tendo o mesmo valor constante em todas as regiões intercelulares. Desde que os resultados obtidos com uma tal aproximação não foram satisfatórios uma melhoria na aproximação da densidade de carga nas regiões intercelulares é necessária. Neste trabalho a densidade de carga ainda é constante fora da esfera inscrita, mas com valores diferentes em cada região intercelular. Uma nova expressão para o momento do dipolo é obtida e aplicada às moléculas diatômicas HF, CO, BF e CS. Além disso as curvas do momento de dipolo, as curvas de energia potencial e as constantes espectroscópicas são calculadas levando em consideração nossa aproximação tradicional para a densidade de carga. Os resultados dos dois modelos são comparados entre si e com os resultados experimentais para todas as moléculas consideradas.