Electric Dipole Moment of Diatomic Molecules

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Abstract The electric dipole moment of some diatomic molecules is calculated using the Variational Cellular Method. The results obtained for the CO, HB, HF and LiH molecules are compared with other calculations and with experimental data. It is shown that there is strong dependence of the electric dipole moment with respect to the geometry of the cells. The possibility of fixing the geometry of the problem by giving the experimental value of the dipole moment is discussed.

1. INTRODUCTION

The motivation to calculate the electric dipole moment for some closed-shell, heteronuclear, diatomic molecules, is not only the important role that this quantity plays is atomic and molecular physics. Although we know that the Intensity in the infrared spectra of a diatomic molecule depends essentially on the variation of the electric dipole moment with the interatomic distance, and that the knowledge of this quantity is crucial in order to compute radiative lifetimes[1], the main reason to study the dielectric dipole moment based on the variational cellular method, is the necessity to have a more rigorous criterion than the one actually in use, (vide section 2 in what follows) to obtain one important parameter in VCM.

This parameter fixes the position of the plane separating the cells that surrounds the atoms of the molecule. Variation of this parameter produces significant changes in the calculated potential curve and consequently in the spectroscopic properties of the diatomic molecule. For an homonuclear diatomic molecule the separating plane passes through the middle of the interatomic distance and of course is perpendicular to the symmetry axis of the molecule. In this case there are no

problems in the determination of the location of the plane. The same does not happen when the molecule is heteronuclear. Given the inter-atomic distance and the localization of the plane, the cells 1 and 2, which encircle the two atoms of the molecule, are complete;y known, according to Figure 1. When the plane moves to the right or to the left the radil of the inscrlbed spheres 1 and 2 of Figure 1 vary. Any mol-ecular property depending on the size of the atoms will consequently vary too.

The molecular electric dipole moment is a physical quantitywith these characteristics and depends strongly on the location of the separating plane. We thought of using the value of this quantity to establish a crlterlon to determine the positlon of the plane along the axis of the molecule: - the position must be such that the calcu-lated dipole moment results as close as posslble to its experimental value.
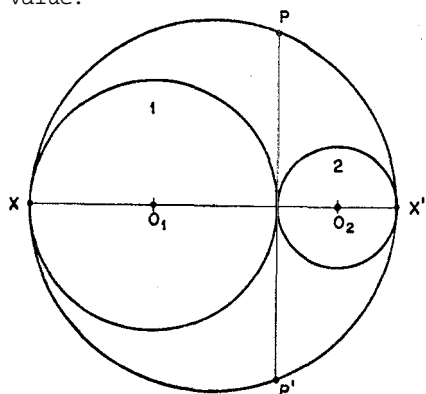

Fig.1 - PP' isthe separating plane. The curved surfaces P X P' and P X' P' are the cells that sur-round the atoms located at O_1 and O_2. The distance O_1O_2 isthe inter-atomic distance.

2. CALCULATION

The mathematical expression for the electrlc dipole moment in the VCM is given in Debye units by[2]

$$\vec{\mu} = 2.541 \left[(Z_2 - Q_2 - \bar{Q}/3)a_1 - (Z_1 - Q_1 - \bar{Q}/3)a_2 \right] \hat{k} \qquad (1)$$

In the above expression Q_1 and Q, are the electronic charges inside the inscrlbed spheres 1 and 2 of Fig. 1, and $\bar{Q}$ Is the total charge in the Intercellular region, that is, in the region located between the cells and the inscribed spheres.

Z_1 and Z_2 are the positive nuclear charges, located at the positions O_1 and O_2 of Fig.1. These charges are not necessarily equal to the number of protons of the atoms 1 and 2, since, to simplify the overall calculations, those electrons that belong to the highly localized states, are incorporated into the corresponding nuclei. Consequently, Z_1 and Z_2 are the net positive charges resulting from the superposition of the protons and incorporated electrons, The electronic charges Q_1, Q_2 and $\overline{Q}$ are given by the number of electrons which are not incorporated into the nuclei. The quantities a_1 and a_2 are the radii of spheres 1 and 2. The numerical factor 2.541 converts the units of the electric dipole moment from the $(e\text{-}a_0)$ units to the Debye units, where 1 Debye $\approx 10^{-18}$ CGS units. The unit vector $\hat{k}$, which goes from O_1 to O_2, rests along the symmetry axis of the molecule.

The calculation of the electric dipole moment with VCM goes through the following sequence of steps.

I) The experiment gives the equilibrium interatomic distance $R_e = \overline{O_1O_2}$ of Fig.1. Yotice that $R_e = a_1 + a_2$. To determine the position of the separating plane along the axis of the molecule, we impose that the ratio a_1/a_2 is proportional to the relation between the covalent radii of the corresponding atoms. Thus, if $(r_c)_1$ is the covalent radius of the atom located at the position O_1 of Fig. 1 and $(r_c)_2$ is the covalent radius of the other atom, then a_1 and a_2 are chosen in such way that

$$a_1/a_2 = (r_c)_1/(r_c)_2 \tag{2}$$

$$a_1 + a_2 = \cdot R_e \tag{3}$$

ii) In VCM the charges Q_1 and Q_2 are determined in the same way. For the molecular orbital a, the probability $P_{i\alpha}$ of the electron being in the cell i, is calculated from equation (30) of Reference 3. Ofcourse, there we have $P_{1\alpha} + P_{2\alpha} + P_{3\alpha} = 1$. Since we know the orbital occupation that is, the maximum number of electrons that the orbital may contain (2 electrons if it is a σ orbital, 4 if it is π, δ etc.) we can compute the fraction of the occupation charge in each cell due to the orbital α. Adding up these fractions for all orbitals, we obtain the total electronic charge in each cell of the problem. Equation (37) of Reference 3 determines the spherically symmetric electronic charge density $N_{i\alpha}(\vec{r})$

at the point $\vec{r}$ inside the inscribed sphere i due to the orbital a. With this quantity one can obtain the electronic charge inside the sphere i due to each orbital a. Adding these values for all orbitals we can get the charges Q_1 and Q_2 of Equation 1.

iii) The electronic charge Q, which is the total electronic charge in the reglon between the cells and the inscribed spheres, can be obtained directly from the charges Q_i already determined above, subtracting the value obtained for the electronic charge in the cell i minus the value obtained for the charge inside the Inscrlbed sphere i. In this way we get charge $\bar{Q}_i$ which added up to all cells gives us the intercellular charge $\bar{Q}$ of Equation (1). In the way we are using the VCM computer program, which corresponds to the geommetry of Figure I, we do not have the intercellular region 3, because the cells 1 and 2 (two calottes, in the case) join continuously and form a unique sphere separated by the plane $\overline{PP'}$, according to Figure 1. In this case the charge $\bar{Q}$ can be obtained directly from the charges Q_i inside the inscribed spheres. The total valence electronic charge Q_T of the atoms of the molecule isgiven by

$$Q_T = (Q_1 + \bar{Q}_1) + (Q_2 + \bar{Q}_2) + (Q_3 + \bar{Q}_3) \qquad (4)$$

Since $\bar{Q}_3 = 0$, because there is no intercellular region 3, we obtain

$$\bar{Q} \equiv \bar{Q}_1 + \bar{Q}_2 = Q_T - (Q_1 + Q_2 + Q_3) \qquad (5)$$

Thismeans thatoncewe know the charges Q_i inside the inscribed spheres we can compute $\bar{Q}$ immediately from the electronic valence charge of the molecule.

3. APPLICATION

A - HF Molecule

We first studied the HF molecule. Some prellminary results concerning this molecule appeared In Reference 2. We now complement those previous results by obtainlng the potential curve of the molecule and determining from this curve the spectroscopical constants of the molecule. This was done only for the HF molecule. In the other cases, VCM was applled only for the experimental equilibrium interatomic distance

R_e, and it was only for this distance that the orbital energies, total electronic energy and dipole moment were calculated.

The HF ground state is the state $X^1\Sigma^+$ which corresponds to the electronic closed shell configuration $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4$. The $1u$ molecular orbital comes from the $1s$ fluorine atomic orbital, which is very tightly bound[4], so the two electrons of this orbital were incorporated into the positive charge $Z = 9$ of the fluorine atom. As a consequence, the total electronic charge Q_T of the HF molecule was considered to be equal to 8 electrons, while the positive charge of the fluorine atom was taken to be equal to 7.

The covalent radii of the atoms of this molecule are $(r_c)_H = = 0.30$ Å aiid $(r_c)_F = 0.64$ Å [5], so the relation between the covalent radii is 0.47. The equilibrium interatomic distance is $R_e = 1.733\, a_0$ [6] and using equations (2) and (3) we can get the radii of the inscribed spheres 1 aiid 2 as $a_1 = a_F = 1.1789 a_0$ and $a_2 = a_H = 0.5541 a_0$. The values of the exchange-correlation parameter α are the ones obtained by Schwarz[7], except for hydrogen, where we use the value $\alpha_2 = \alpha_H = 0.7723$. With these input data For the VCM program, the values of the charges Q_1 and Q_2 inside the inscribed spheres around the fluorine and hydrogen atoms were obtained, with resulting values $Q_1 = 4.883$ and $Q_2 = 0.112$, (in units of electron charge). For the intercellular charge $\bar{Q}$ the value obtained is $\bar{Q} = 1.556$, in the same unit as above. Substituting these data into equation (1) the obtained value for the èlectric dipole moment is $\vec{\mu} = = -1.14\, \hat{k}$ debye. According to our notation the unit vector $\hat{k}$ is directed from the center of the inscribed sphere 1 to the center of sphere 2, that is, from the fluorine to the hydrogen atom. The above result tells us that the vector dipole moment is a vector directed from the hydrogen to the fluorine atom. However, this is not the correct sense of this vector for this molecule, according to other more rigorous calculations. Besides giving the wrong sign for the vector dipole moment the input data used above also gives a too small magnitude for this vector.

To improve these results we changed the way of choosing the radii of the inscribed spheres. Let us consider that the ratio a_1/a_2 is not only proportional to the ratio of the covalent radii, but it is also proportional to the electronegativity of the atoms of the molecule. In this way, instead of using equation 2, iet us use the equation

$$a_1/a_2 = (r_c)_1 \, f_1/(r_c)_2 \, f_2 \tag{6}$$

where f_i is the electronegativity of atom i. Since $f_1 = f_F = 4.0$ and $f_2 = f_H = 2.1$ the relation a_1/a_2 now becomes equal to 0.24. Combining with the experimental value $R_e = 1.733a_0$, we obtain a, $= 1.3976\,a_0$ and $a_2 = 0.3354a_0$.

   With these new values of the radii of the inscribed sphere, with all the others parameters fixed, VCM gives for the electronic charges $Q_1 = 5.819$, $Q_2 = 0.017$, and $\bar{Q} = 0.846$, in units of electron charge. Taking these values into eq. (1), the electric dipole moment results equal to $\vec{\mu} = 1.72$ $\hat{k}$ Debye. The vector $\vec{\mu}$ now points to the right direction and also has a magnitude in excellent agreement with other calculations, and with the experimental result $(\mu_{expt} = 1.73$ Debye$)$[8].

   Due to the fact that new values of a, and a_2, and consequently, the new position of the separating plane, give such an excellent result for the electric dipole moment, we decided to test whether the same improvement would occur with other physical quantities associated with this parameter. In Table I the orbital energies of the HF molecule are presented.

Table I - Orbital energies of the HF molecule, in Rydberg, for the internuclear distance $R_e = 1.733$ a_0

	HF[a]	LCAO[b]	MCV[c]	MCV[d]
1σ	- 52.59	- 52.28	- 48.53	- 48.46
2σ	- 3.20	- 2.95	- 2.19	- 2.17
3σ	- 1.54	- 1.13	- 0.95	- 0.83
1π	- 1.30	- 0.93	- 0.82	- 0.83

a) See ref. 9. b) See ref. 8. c) Position of separating plane according to eq. (2). d) Position of separating plane according to eq. (6).

The results that appear in the first two columns of Table I are a SCF-LCAO calculation and those in the last two columns are the orbital energies for the two positions of the separating plane PP'.

   Numerical values corresponding to some paints of the potential

curve were also obtained for the two positions of the separating plane. The results for several valueç of the interatomic distance are given in Table II, together with results of a Hartree-Fock calculation.

Table II - Numerical values of the potential curve of the HF molecule, in Rydberg, for the two positions of the separating plane

$R(a_0)$	HF (a)	Energy (b)	Energy (c)
1.00	-	- 200.8012	- 200.5229
1.20	-	- 200.4239	-
1.40	-	- 200.4853	- 201.1201
1.50	- 200.1053	- 200.5014	- 201.1258
1.60	-	- 200.5165	- 201.1183
1.733	- 200.1406	- 200.5131	- 201.0742
1.80	- 200.1346	- 200.5110	- 201.0485
1.90	-	- 200.5084	- 201.0039
2.00	-	- 200.4723	- 201.9551

a) See ref. 9. b) The position of the separating plane is given by eq. (2). c) The position of the separating plane is given by eq. (6).

        Once the potencial curve is obtained, some spectroscopical constants of the molecule, such as vibrational constant ω_e, dissociation energy D_e, equilibrium interatomic distance R_e etc., can be determined imediately. The theoretical value of R_e is the value of R for which the potential curve is a minimum. From Table II it is easy to verify that $R_e = 1.60a_0$ for the situation a of that Table, and it is equal to $R_e = 1.50a_0$ for the other position of the separating plane. The dissociation energy is the energy which corresponds to the difference between the total energy of the atoms when infinitely separated and the energy at the equilibrium position. The energy of the atoms H and F when they are far apart is given by - 199.8186 Ry [10]. Thus the dissociation energy in the case a of Table II is given by 9.49eV, while for the situation b it is equal to 17.78eV. The experimental value of this energy is 6.40eV [11]. The vibrational frequency of the ground state of the HF

molecule can be obtained from the continuous curve that can be drawn from Table II. A parabola is adjusted to fit this continuous curve and if A is the second order coefficient of the adjusted parabola, it is known that the vibrational frequency ω_e and A are connected by the relation ¹ "

$$2A = 5.8883 \times 10^{-2} \mu \omega_e^2 \text{dyn/cm}$$

where μ is the reduced mass of the molecule. In this way we obtain for o_e the values 4262cm^{-1} and 3915cm^{-1} for the cases a and b of Table II respectively. The experimental result for the vibrational frequency is 4138cm^{-1}. In Table III all the spectroscopical constants discussed above are listed together with the experimental results.

Table III - Spectroscopic constants of the HF molecule

	MCV (a)	MCV (b)	Expt. (c)
$R_e(a_0)$	1.60	1.50	1.733
D_e (eV)	9.49	17.78	6.40
ω_e (cm^{-1})	4262	3915	4138
E (d)	- 200.5165	- 201.1258	- 201.0540

a) The position of the separating plane is given by eq. (2). b) The position of the separating plane is given by eq. (6). c) See ref. (1.1). d) For $R = R_e$.

B - Other Molecules

We have also studied the BH, CO and LIH molecules. The calculations were performed for the experimental equilibrium internuclear distance only. The electric dipole moment of these molecules were calculated for the two positions of the separating plane.

The ground state of the BH molecule is the state X $^1\Sigma^+$ which corresponds to the closed shell electronic configuration $1\sigma^2 2\sigma^2 3\sigma^2$. The covalent radii of the atoms of this molecule are $(r_c)_1 = (r_c)_B = 0.88 \text{Å}$ and $(r_c)_2 = (r_c)_H = 0.30 \text{Å}$ [5]. The relation between these covalent

radii is 2.933. The experimental equilibrium distance is R_e = 1.2325 $\overset{\circ}{A}$, so that eq. (2) gives the values $a_1 = a_B = 1.7375a_0$ and $a_2 = a_H = 0.5924$ a_0. If the electronegativity of the atoms is taken into consideration according to eq. (6) the relation a_1/a_2 becomes equal to 2.7933 and the radii a_1 and a_2 of the inscribed spheres result equal to $1.7157a_0$ and $0.6142a_0$, respectively. In Table IV the results of the calculations for the BH molecule are presented.

Table IV - Value of the charges, orbital energies (in Rydberg), dipole moment (in Debye) of the BH molecule

	MCV[a]	MCV[b]	LCAO[c]
Q_1	1.496	1.441	-
Q_2	0.180	0.206	-
$\bar{Q}$	0.950	0.982	-
1σ	- 13.33	- 13.34	- 15.50
2σ	- 0.84	- 0.85	- 1.30
3σ	- 0.43	- 0.43	- 0.69
E[d]	- 50.4044	- 50.4098	- 50.1242
μ	0.44	0.11	0.99

a) The position of the separating plane is given by eq. (2). b) The position of the separating plane is given by eq. (6). c) See ref.8. d) For R = R_e = 2.3299 a_0.

The ground state of the CO molecule is the state X $^1\Sigma^+$ which corresponds to the closed shell electronic configuration $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 4\sigma^2 5\sigma^2$. The covalent radii of the atoms of this molecule are given by: $(r_c)_1 = (r_c)_C = 0.772$ $\overset{\circ}{A}$ and $(r_c)_2 = (r_c)_O = 0.66$ $\overset{\circ}{A}$ [5]. The relation between the covalent radii is equal to 1.1698, and since the internuclear distance is given by $2.1320a_0$, the values a_1 and a_2 are $1.1494a_0$ and $0.9826a_0$, respectively. These radii, however, become equal to 1.1615 a_0 and $0.9705a_0$, respectively, when the electronegativity of the atoms are taken into consideration according to equation (6). The VCM results

for this molecule using these two positions of the separating plane are shown in Table V.

Table V - Value of the charges, orbital energies (in Rydberg), dipole moment (in Debye) for the two positions of the separating plane and for other theoretical and experimental results related to CO molecule

	MCV[a]	MCV[b]	LCAO[c]	Exp.[c]
Q_1	1.417	1.508	-	-
Q_2	2.946	2.829	-	-
$\bar{Q}$	3.336	3.360	-	-
1σ	- 37.60	- 37.63	- 41.42	-
2σ	- 20.06	- 20.04	- 22.71	-
3σ	- 1.85	- 1.84	- 3.00	-
4σ	- 1.04	- 1.04	- 1.46	-
1π	- 0.84	- 0.82	- 1.17	-
5σ	- 0.52	- 0.53	- 0.96	-
E[d]	- 226.0243	- 225.9879	- 224.6872	- 226.7540
	1.99	2.68	0.73	0.11

a) The position of the separating plane is given by eq.(2). b) The position of the separating plane is given by eq, (6). c) See ref. 8. d) For $R = R_e$ = 2.132 a,.

The ground state of the LiH molecule is the state $X^1\Sigma^+$ which corresponds to the eiectronic configuration $1\sigma^2 2\sigma^2$. The covalent radius of the atom Li is equal to $2.5255a_0$ and of the H is the same as given previously. This makes the relation between them equal to 0.2776. The experimental vaiue of the internuclear distance is $3.015a_0$, so the radii of the inscribed spheresresult equal to $2.3599a_0$ for Li and 0.6551 for H. These values turn out to be $1.9046a_0$ and $1.1104a_0$, respectively, if the electronegativity of the atoms are used. The VCM results for the LiH

molecule using the two sets of values for the radii of the inscribed spheres are! presented in Table VI.

Table VI - Values of the charges inside the spheres, orbital energies
(in Rydberg) and dipole moment (in Debye) of the LiH mol-
ecule

	MCV[a]	MCV[b]	LCAO[c]	Expt.[c]
Q_1	2.378	2.095	-	-
Q_2	0.119	0.607	-	-
$\bar{Q}$	0.626	0.775	-	-
1σ	- 3.82	- 3.72	- 4.89	-
2σ	- 0.37	- 0.39	- 0.61	-
E[d]	- 15.8889	- 15.9128	- 15.8332	- 16.1404
μ	3.34	- 1.14	6.41	5.88

a) The position of the separating plane is glven by eq. (2). b) The pos-
itlon of ttie separating plane is given by eq. (6). c) See ref. 8.   d)
For $R = R_e = 3.015$ a,.

4. CONCLUSIONS

The position where the separating plane cuts the symmetry axis of tht: molecule is a very important parameter in VCM calculations. Not only the radii of inscribed spheres which surround the atoms of the molecule depend on this paramter, but the charge inside the spheres, the electric dipole moment, etc., depend on it too.

For the CO molecule, for instance, we can see from Table V, that a variation of 1% in the radius of the inscribed sphere 1, results in a variation of 6% of the charge inside this sphere. The corresponding variation in the electric dipole moment is 35%. For the BH molecule, moreover, the same variation in the radius of the first sphere produces a variation of 4% in the charge Q_1 and a 75% variation in the electric dipole moment. What is more impressive, however, is what happens with the LiH molecule. A change of 20% in the radius of the flrst sphere and

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70% in the radius of the second sphere produces a change of 630% in the electric dipole moment. These observations are useful to call attention to the strong dependence of the electric dipole moment on the value to the radius of the inscribed sphere. Other quantities, like the total energy, do not show such a strong dependence on the location of the plane. The energy of the orbitals is also approximately independent of this parameter, as can be seen from Tables I to VI.

While the choice of the position of the separating plane made according to eq. (6) gives excellent result for the electric dipole moment of the HF molecule, the same does not happen with the LiH molecule. For this molecule the best size of the radii of the inscribed spheres are the ones that result from the use of eq. (2), instead of eq. (6) . Even for other molecular properties of HF which depend on the location of the separating plane, such as dissociation energy, equilibrium internuclear distance, etc., seem to get better values when the position cf the separating plane is fixed according to eq. (2).

We can conclude that if the choice of the position of the separating plane made according to the ratio of the covalent radii of the atoms is not a good choice, the choice made according to eq. (6), is still worse specially for the molecules HF, BH, CO and LiH.

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Resumo

O momento de dipolo elétrico de algumas moléculas diatômicas é calculado usando o Método Celular Variacional. Os resultados obtidos para as moléculas CO, HB, HF e LiH são comparados com outros cálculos e com os resultados experimentais. Mostra-se que há uma forte dependência do momento de dipolo elétrico com a geometria das células. Discute-se a possibilidade de se fixar a geometria do problema dando o valor experimental do momento de dipolo.